COTTON-CELLUL(

ITS CHEMISTRY AND TECHNOLO

BY

A. J. HALL, B.Sc., F.I.C., F.C.S.

(DYERS' COMPANY RESEARCH GOLD MEDAL)

Chief Chemist
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PREFACE

ALTHOUGH numerous books exist dealing with various phases of cellulose chemistry, it is difficult to find an up-to-date English book treating of this subject in a comprehensive, yet concise, manner, and this book is written to remedy this defect.

During the past few years, the application of cellulosic materials has increased tremendously, and partly because of this and partly because of the increased amount of research now devoted to cellulose, our knowledge of this important material has been greatly increased

An attempt is made, in the present volume, to present a readable but informative account of present-day knowledge of cellulose, particularly of cotton-cellulose The main lines of recent researches have been indicated and the results obtained so far are discussed. It is hoped that any one wishing to obtain an accurate and comprehensive idea of the essentials of modern cellulose chemistry and technology will find this book useful.

In the preparation of this book I have received much valuable assistance. Messrs. Sir J Farmer, Norton & Co. Ltd ; The Longclose Engineering Co. Ltd. ; Spencer and Sons Ltd and Jackson and Brother Ltd —textile engineering firms of world-wide reputation—have kindly supplied blocks of various bleaching and dyeing machines, and The British Cotton Industry Research Association and The Linen Industry Research Association have generously supplied numerous blocks relating to investigations carried out in their Research Institutes.
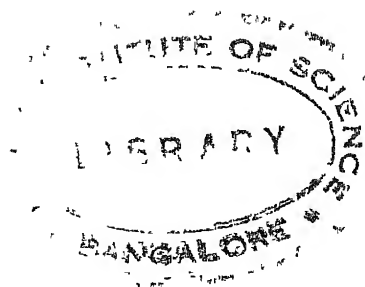
The loan of several blocks of figures published in the *Journal of the Textile Institute* has been obtained through the courtesy of the editor—Mr Hugh L. Robinson—and The Society of Dyers and Colourists have loaned the blocks for Figures 45, 46, 47, 48, 49, 50, 51, 52 and 53.
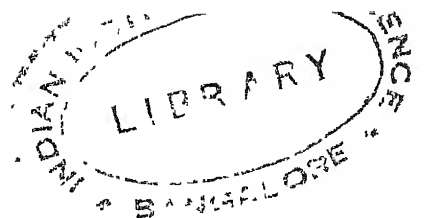
Mr. C H W. Vivian, B Sc., A I C , and Mr. F. C Wood, B Sc., F.I.C., have given much assistance, and Principal J C Irvine of the University of St. Andrews and Dr S Judd Lewis have kindly read the proofs of those portions of the book in which their investigations on cellulose are described.

<div align="right">A. J HALL.</div>

October 1924

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ERRATA

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Page 206, *for* Table CXI *read* Table CX

▰▰▰▰▰▰▰▰▰▰▰▰ generally carried out
is follows
The land is ploughed in much the same manner as is arable land in
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hree months the red and white cotton flowers are in full bloom, and these
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ɔ thirty-six seeds, to which the cotton hairs (about 8000) are attached. Later

3   25

COTTON-CELLULOSE

CHAPTER I

COTTON AND CELLULOSE

COTTON represents the purest type of cellulose produced in nature, containing as it does about 90 per cent. of pure cellulose. Flax, ramie, hemp and other fibres also contain a high proportion of pure cellulose. On the other hand, wood and cereal straws are distinguished as containing smaller quantities of cellulose which are also intimately associated with lignin Natural fibrous materials may therefore be arbitrarily classified as follows

	Cellulose Content
Cotton	90 per cent.
Coniferous woods . . .	60 ,,
Cereal straws . . .	30–40 ,,

It would be extremely convenient to consider that the pure celluloses isolated from these fibrous materials were identical, and various investigators have now brought forward considerable evidence to show that this is actually true in fact Cellulose, however, is a colloidal substance whose molecule consists of the complex $(C_6H_{10}O_5)_n$ It is therefore evident that the physical and chemical properties of such a substance may be considerably modified during its extraction from cellulosic materials without detracting from its purity Hence it is always likely that pure celluloses isolated from various sources will always differ in some of their properties

The chemistry of wood, flax and other cellulosic substances has recently extended so considerably that it has not been found possible to deal here with these substances in detail , but most of the information contained in this book on cotton-cellulose is applicable to cellulosic materials of all kinds.

The cotton plant is grown in tropical regions and, though it is a perennial, it is usually treated as an annual shrub. Its cultivation is generally carried out as follows

The land is ploughed in much the same manner as is arable land in Europe, and the cotton seed is sown in ridges about 5 feet apart. After about one week the young plants, which are susceptible to frost, appear, and are then thinned so that they stand about 15 inches apart. In about three months the red and white cotton flowers are in full bloom, and these subsequently die and give place to cotton bolls, each containing thirty-two to thirty-six seeds, to which the cotton hairs (about 8000) are attached. Later

the bolls mature, ripen, and burst, exposing a fluffy mass of white cotton which is picked, freed from the seeds by ginning, and afterwards baled and made ready for transport.

Many types of cotton are known and cultivated, the most important being :

> Sea Island Cotton (American).
>   ,,   ,,   (Egyptian).
>   ,,   ,,   (Queensland).
> Ordinary Orleans of America.
> Indian.
> Egyptian.
> Brazilian.
> West Indian.
> East Indian.
> West African.

Cotton may also be classified according to its staple (that is, the length of the cotton hairs)—long, medium, and short staples being generally recognised thus

TABLE I

Staple	Length of Cotton Hair.	Origin of Cotton
Long . . .	$1\frac{1}{2}$–$1\frac{1}{4}$ inches	Sea Island, Egyptian Improved Uplands
Medium. . .	1–$\frac{3}{4}$ inch .	Ordinary American Upland.
Short . . .	$\frac{5}{8}$–$\frac{3}{8}$,,	Mostly East Indies.

At the present time (*Textile Manufacturer Year Book*, 1923), about 60 per cent. of the world's supply of cotton is grown in America, 18 per cent. in India, 6 per cent. in Egypt, 4 per cent. in Russia, 4–10 per cent. in China, and 5 per cent in Brazil, and other countries. The following varieties of cotton and their chief characteristics are also noted in Table II. opposite.

The structure of cotton hairs is described in detail by Bowman (*The Structure of the Cotton Fibre*), Denham (*Journ. Text Inst.*, 1922, xiii. 99 ; 1923, xiv 86), and by Balls (*The Development and Properties of Raw Cotton, etc*), and is illustrated in Fig. 1. It is seen that each hair grows outwardly from the seed to which it is attached (vii and viii), and is distinguished as containing an outer primary wall, which in the ripe hair is known as the cuticle. As growth continues a secondary thickening develops within the primary wall, and this may be normal (iva) or supernormal (ivb), or perhaps it may even be absent (ivc). Within

TABLE II

Origin.	Variety.	Average Length.	Average Diameter.	Notes.
AMERICA	Sea Island	1·8 inches	0·0005 inches	A fine silky variety
	Florida Sea Island	1·6 "	0·0006 "	The best and most regular American cotton
	Orleans	1·05 "	0·00075 "	} Soft clean cottons
	Upland	1·0 "	0·0008 "	
	Mobile	1·05 "	0·0008 "	
	Texas	1·0 "	0·0008 "	Firmer in staple than the above
	Sakellaridis	1·6 "	·	A fine long staple; creamy white colour
EGYPT	Mitaffi	1·4 "	0·00065 "	Rich brown fibre, long and fine
	Johanorich	1·5 "	0·0006 "	A fine white silky cotton.
	Abassi	1·4 "	0·0006 "	A fine white cotton
	Brown	1·25 "	0·00065 "	Harsher than the five varieties above.
	White	1·2 "	0·0007 "	Light brown in colour; strong staple
	Uppers	1·37 "	··	
BRAZIL	Pernams	1·25 "	0·00075 "	
	Maranhams	1·05 "	0·0007 "	
	Paraiba	1·15 "	0·0007 "	
	Ceara	1·1 "	0·0007 "	
	Maceo	1·15 "	0·0007 "	
	Hinghunghat	1·05 "	0·0008 "	
	Dhollerah	0·9 "	0·0008 "	
	Tinnevelly	0·9 "	0·0008 "	
	Broach	0·9 "	0·0008 "	
INDIA	Comptah	0·9 "	0·0008 "	Some of the lower varieties contain much dirt and unsuitable fibres.
	Bengal	0·8 "	0·0008 "	
	Scinde	0·7 "	0·00085 "	
	Surat	0·8 "	0·00085 "	
	Madras	0·75 "	0·00085 "	
PERU	Sea Island	1·5 "	0·0006 "	A soft silky cotton; long in staple.
	Smooth	1·15 "	0·0007 "	Similar to Orleans.
	Rough	1·05 "	0·0008 "	Similar to Brazilian cottons.
WEST INDIES	West Indian	1·2 "	0·00075 "	Length of staple variable
GREECE	Smyrna	1·1 "	0·0007 "	Harsh in staple, irregularly twisted.
AFRICA	Lagos	1·0 "	0·0008 "	

the hair, and containing the nucleus responsible for its growth, is a central canal or lumen (v). Subsequently the hair ripens, loses much of its moisture content by evaporation, and becomes like a twisted ribbon, which is modified as the secondary thickening is normal (1), supernormal (2), or absent (3) The primary wall or cuticle is also marked by numerous pits and spiral striations which have formed the basis of considerable discussion as to the growth of the hair

Investigation of the growth of the secondary thickening has led Balls to conclude that it is formed of successive layers of cellulose which are laid down on successive days of growth Balls (*Phil Trans*, 1915B, 1915), from observation of the growth of cotton in Egypt, noted that the cotton seed hairs are of two kinds—lint (the normal cotton hairs), and short lint (fuzz hairs—much shorter and thicker than normal cotton hairs, and having fewer convolutions), and that the growth of both was arrested each midday. Since the period of growth is about 21–25 days, it appears likely that these cessations of growth may give rise to a corresponding number of layers, and Balls calculated that it would be necessary to magnify the distance between these growth layers or rings about five times in order to render them visible

0 2 g of lint or fuzz was boiled out with 1 per cent caustic soda, afterwards acidified with dilute acetic acid and thoroughly washed and dried The cotton was then placed in vacuo and impregnated with 3 c c of 9 per cent caustic soda and then with 3 c c. of carbon disulphide After a few hours', or maybe a day's, standing, the consequent swelling of the lint or fuzz enabled the growth rings to be observed under a magnification of 250 diameters, and the cotton hairs had an appearance shown in Fig 1 (x).

Balls found that with lint the number of rings never exceeded 25 and was not less than 20; the number of growth of rings in fuzz was usually more than 16. The thickness of each ring was about $0\cdot4\mu$. It therefore appears to be proved that cotton hairs are made up of a number of concentric layers of cellulose bounded by a cuticle which may or may not be composed of the same cellulose but which contains fatty matters

Convolutions.

As previously indicated, cotton hairs are twisted, and the nature of these twists or convolutions has recently been re-investigated by Clegg and Harland (*Journ Text Inst.*, 1924, xv 14) In each cotton hair there are frequent reversals in the convolutions, and it is therefore of interest to know the number of convolutions and their reversals per unit length of hair

Clegg and Harland observed the following facts concerning the number of convolutions per mm in different types of cotton, shown on Table III page 30, from which it is seen that the frequency distributions of convolutions per mm. among the hairs examined, varied from 3·9 to 6·5.
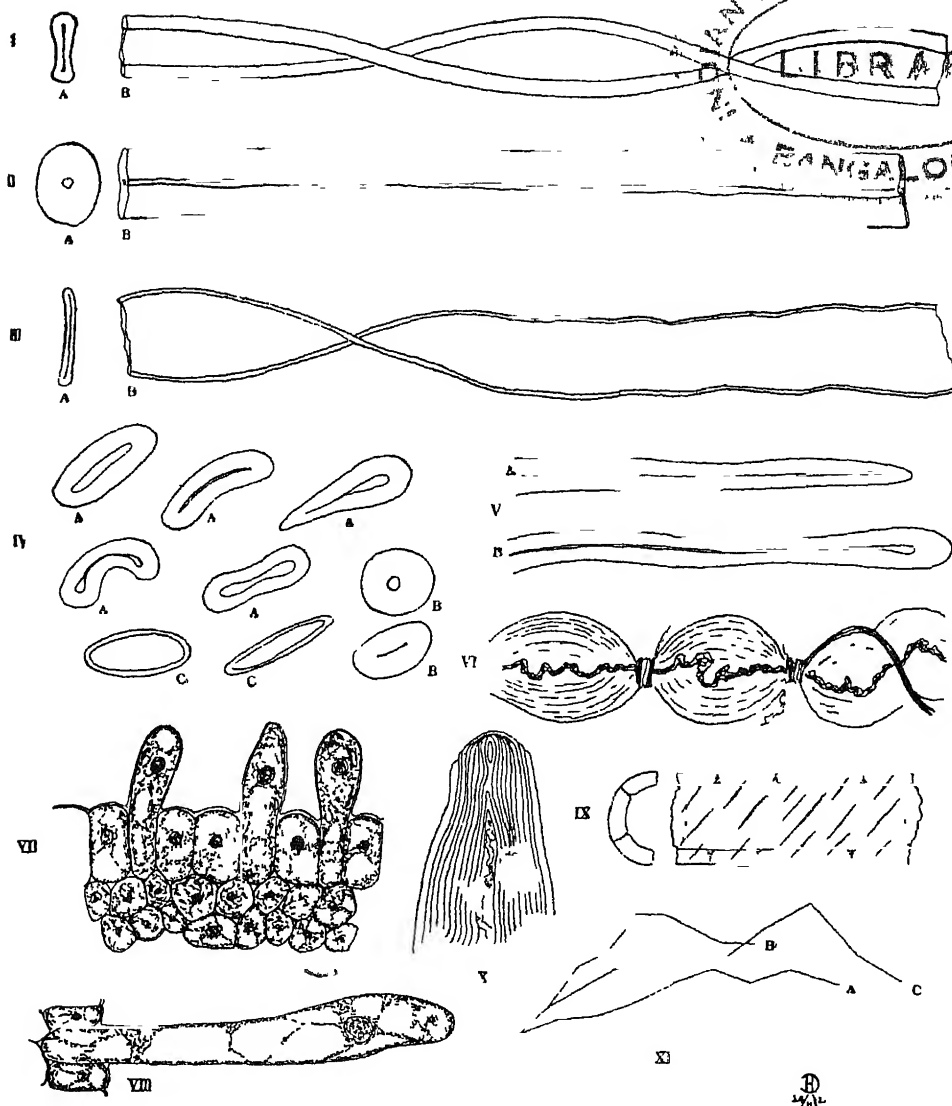
FIG 1—STRUCTURE OF COTTON HAIRS.

I   Normal hair × 500, showing convolutions and thickened edge
II Supernormally thickened hair, showing absence of convolutions and small central canal, × 500
III Immature and thin walled hair
IV. Cross-sections   A, normal , B, supernormal thickening , C, thin walled , × 500
V. Tips or tails of cotton hair, showing small diameter of hair and central canal   A, acuminate , B, spatulate   Drawn to scale as preceding figures.   Complete hairs drawn to this magnification would be 25 metres long
VI Typical appearance of hair under treatment with "caprammonium" showing "beading" and bands of cuticle, also suggestion of "growth rings" , × 200
VII Development of hair from seed coat   Day after opening of flower, × 350
VIII Ditto   Three days later
IX Pits in wall of hair   (After Balls.)
X   Growth rings at tip of cotton hair.   (Balls)
XI Hair conformations, from data by Wiesner , schematic representation, length × 1 66, diameter × 430 from cross-sections   A, *G. herbaceum* , B, *G. flavidum* , C, *G. conglomeratum*

TABLE III

Convolutions per mm.

Cotton	0.	1.	2.	3.	4.	5.	6	7.	8	9	10	11.	12.	Mean
Trinidad . . .	–	1	3	6	12	14	6	2	3	–	–	1	–	4·8
Indian . . .	–	–	–	7	11	17	10	3	–	–	–	–	–	4·8
,, . . .	–	–	–	3	10	13	8	8	3	2	1	–	–	5·6
Sea Island . . .	–	1	4	13	15	12	2	1	–	–	–	–	–	3·9
Upland Sea Island .	–	–	–	–	2	7	18	10	8	1	2	–	–	6·5
Egyptian . . .	–	–	–	4	4	16	13	10	1	–	–	–	–	5·5
Upland . . .	–	–	1	9	14	11	12	1	–	–	–	–	–	5·5

It was further shown that the number of reversals per mm. varied from 1·0 to 1·7, and the ratio of convolutions to reversals from 2·8 to 5·2.

TABLE IV

Cotton.	Reversals per mm. (Average)	Ratio : Convolutions. Reversals. (Average.)
Trinidad	1·4	4·8
Indian	1·0	5·2
,, . . .	1·7	3 8
Sea Island	1·5	2·8
Upland Sea Island . .	1·7	3·9
Egyptian	1·6	3·5
Upland	1·5	3·8

Generally the number of left-handed convolutions is greater than the number of right-handed ones.

The effect of wetting, boiling and tension on the number of convolutions was observed, the results incorporated in Figs. 2, 3 and 4, where a left-handed convolution is shown thus \ and a right-handed convolution thus /.

On wetting, the number of convolutions and reversals is reduced, but on drying the hair returns practically to its original form.

After boiling for 30 minutes at 20 lb. pressure, the hairs were much swollen and translucent, each hair having lost its lumen and almost all its convolutions. On drying, the hairs returned to their original forms.

Under tension, a cotton hair behaves much like a spring, which returns to its natural form when the tension is released.

A = DRY
B = WET
C = RE-DRIED
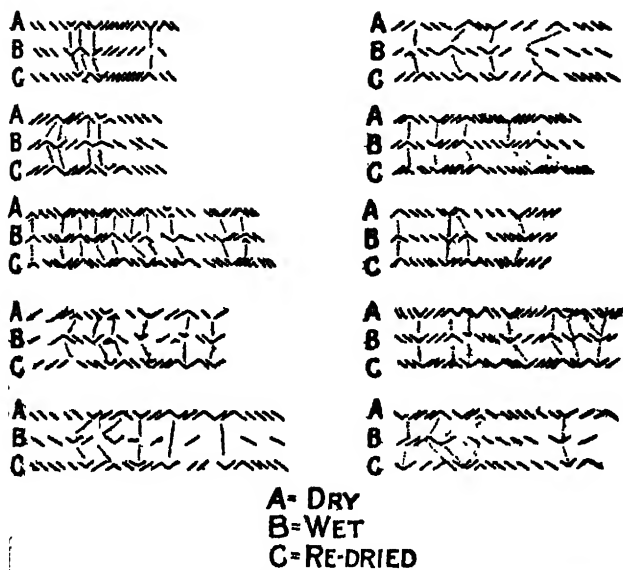
FIG. 2.—EFFECT OF WETTING ON THE NUMBER AND POSITION
OF CONVOLUTIONS.
(Clegg and Harland.)

A = BEFORE TENSION   B = AFTER TENSION   C = ON RELEASE OF TENSION
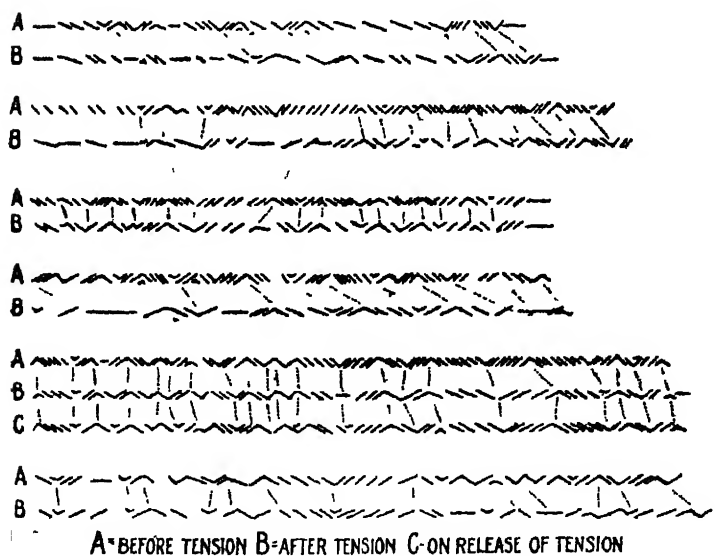
FIG. 3.—EFFECT OF BOILING IN WATER IN AN AUTOCLAVE ON
THE NUMBER AND POSITION OF CONVOLUTIONS.
(Clegg and Harland)

A=BEFORE BOILING   B=AFTER BOILING   C=ON REDRYING
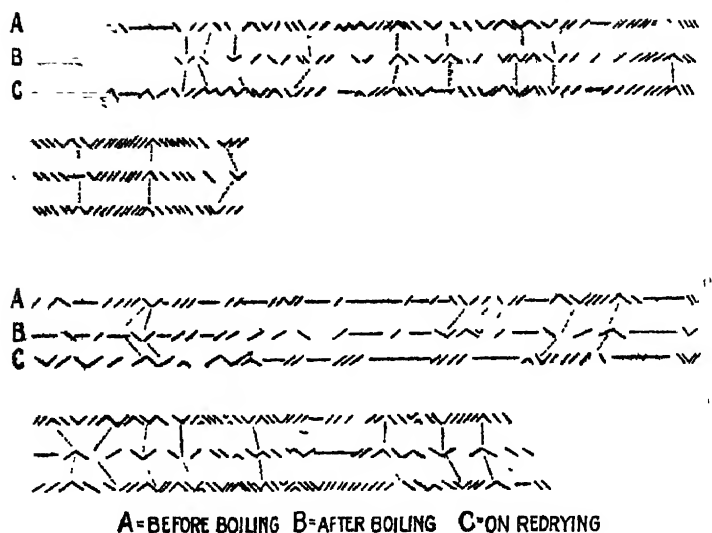
FIG. 4 —EFFECT OF TENSION ON THE NUMBER AND POSITION
OF CONVOLUTIONS.
(Clegg and Harland)

Cross-Section and Tensile Strength.

Accurate measurement of the cross-sectional area of cotton hairs is not possible owing to the distortion which is known to occur under the conditions by which the section is obtained   Clegg and Harland (*Journ Text Inst* , 1923, xiv. 489), and Clegg (*Journ. Text Inst* , 1924, xv 1), however, have obtained data which are useful for comparative purposes, and which may be considered as an approximation to the truth.   This data is incorporated in the following table, together with observations on the tensile strength

TABLE V

Cotton.	Breaking Load of Single Hair.	Area of Cross-Section. Unit = μ^2	Apparent Density (Calc)	Tensile Strength Dynes per cm ^{2}
Sea Island .	5·7 g	122·5	0 84	$4 5 \times 10^9$
,, .	5 8	130·0	0 89	4·3
,, .	5·9	143·5	0 84	4·0
,, .	5·3	130	0 79	4·0
,, .	5·8	146·5	0 77	3·8
,, .	5·3	134 5	0 81	3·8
Egyptian .	5 9	173	0 92	3·3
Sea Island .	5·6	145	1·05	3·8
Peruvian. .	6·4	271	0 83	2·3
Texas .	5·6	245	0·93	2·2

Clegg concluded that diameter is not a measure of strength, but that in any given variety of cotton the strength can be correlated to the wall thickness. It is suggested that the percentage of hairs which break at loads below $1\cdot5$ g. be taken as an index of the amount of thin-walled (so called dead) cotton.

In the above table the apparent density is calculated from measurements of the cross-section and the hair weight per centimetre. By ordinary methods, however, the density of cotton is accepted as $1\cdot50-1\cdot53$. The difference between the calculated and observed values is ascribed to the porosity of the cotton, evidence of which has been obtained from other investigations. By simple calculation, it appears that the pore space in cotton varies from 32–41 per cent. in those cottons actually observed

In another communication, Pierce (*Journ. Text. Inst*, 1923, xv. 1) has found that cotton hairs of all kinds have an approximately constant volume of cellulose which is independent of the staple length, and he gives the following table, which is sufficiently accurate to enable several calculations relating to cotton hairs to be made

Staple length . . .	L cms.
Hair mass	$5\cdot8\times10^{-6}$ g.
Mass per cm . . .	$(5\cdot8/L)\times10^{-6}$ g.
Wall cross-section . . .	$(3\cdot9/L)\times10^{-6}$ sq cms.[1]
Breaking load . . .	$20/L$ g.

The structure and physical properties of cotton hairs would appear worthy of further study, particularly from the point of view of the spinner and weaver, but in the following chapters it will be necessary to deal almost exclusively with the chemistry of cotton

[1] Density of cotton taken as 1 51.

CHAPTER II

RAW COTTON AND ITS PURIFICATION

RAW cotton contains about 90 per cent. of pure cellulose, natural colouring matters, 8 per cent. of moisture, 0·2–0·4 per cent. of nitrogen, 0·5 per cent. of wax, fat and resin, and 1 per cent. of mineral matter, the actual amounts of these substances being determined largely by the type of cotton, its origin of growth and the stage of its maturity.

Nitrogen.

The nitrogen content of raw cotton has been investigated by Ridge (*Journ. Text. Inst.*, 1924, xv. 94), and some typical results are given here .

TABLE VI

Type of Cotton.	Average Nitrogen Content.
Egyptian (Sakellaridis)	0 317 per cent.
,, ,, ...	0 314 ,,
,, (Best Uppers)	0·290 ,,
,, (Uppers)	0·292 ,,
American (Texas)	0·204 ,,
,, (Long Staple Upland) . . .	0·204 ,,
,, (Georgian)	0·221 ,,
Sea Island (West Indian). . . .	0·285 ,,
,, ,, ...	0·272 ,,
,, ,, ...	0·262 ,,
,, ,, ...	0·266 ,,
Indian (Bengal)	0·241 ,,
,, (Surtee)	0·280 ,,
,, (Oomra)	0·180 ,,
,, (Broach)	0·266 ,,
Peruvian (Mitafifi)	0·254 ,,
,, (Tanguis)	0·216 ,,
,, (Fine Smooth)	0·246 ,,
Brazilian (Pernam)	0·260 ,,
,, (Ceara)	0·221 ,,
,, (Musgrave)	0·277 ,,

The nitrogen content of cotton has been also investigated by Schwindler

(*Journ Soc. Dyers & Col*, 1908, xxiv. 106), Knecht and Hall (*Journ. Soc. Dyers & Col.*, 1918, xxxiv 220), Higgins (*Journ. Soc. Dyers & Col.*, 1919, xxxv. 169) and Hebden (*Journ Ind. Eng. Chem.*, 1914, 714), and their results confirm those given above, but for Egyptian and American cottons the nitrogen contents are distinctly lower.

It is noteworthy that the nitrogen content of raw Egyptian cotton is about 0.3 per cent. as compared with 0.2 per cent for American cotton. Moreover, cotton grown in Arizona from Egyptian seed retained its characteristic high nitrogen content—0.399 per cent.

Immature cotton contains more nitrogen than mature cotton, thus :

TABLE VII

Type of Cotton.		Nitrogen Content.
Egyptian,	combed sliver.	0.228 per cent.
,,	comber waste	0.274 ,,
Sea Island,	combed sliver	0.209 ,,
,,	comber waste	0.306 ,,

for the comber waste, obtained by the mechanical operation of combing, contains more immature cotton hairs than the combed sliver.

Practically nothing is known of the manner in which nitrogen is combined within the cotton hairs, though it probably exists in protein matters.

Fats and Waxes.

The wax content of raw cotton has received investigation since the experiments of Schunk (*Mem. Manchester Lit. Phil Soc.*, 1871, xxiv. 95), who obtained a brittle waxy solid by boiling 500 lb. of cotton yarn with a strong solution of sodium carbonate for about $7\frac{1}{2}$ hours and adding sulphuric acid to the resulting dark brown liquor. The wax had the following composition

Carbon . . 80.38 per cent.
Hydrogen . . 14.51 ,,
Oxygen . . 5.11 ,,

it fused at 186.8° F (86° C) and re-solidified at 179.6° F (82° C.) A fatty acid, shown to have the formula, $C_{34}H_{34}O_4$, and thus agreeing with margaric acid, but thought to be a mixture, probably of stearic and palmitic acids, was found to accompany the above wax in small quantity

Subsequently, Knecht and Allan (*Journ Soc. Dyers & Col.*, 1911, xxvii. 142) and Knecht and Streat (*Journ. Soc. Dyers & Col.*, 1923, xxxix 73) have, among

others, investigated the properties of cotton wax, but the most recent and exhaustive investigation has been made by Fargher and Probert (*Journ. Text. Inst.*, 1923, xiv. 49)

Fargher and Probert had for examination the extract obtained by the solvent extraction of about 2 tons of American cotton sliver with commercial 90 per cent. benzol (redistilled before use) During the extraction, the cotton and solvent were heated together by means of live steam at 40 lb pressure, and the extraction occupied about 6 hours The crude semi-solid extract (about 8 lb) contained water and volatile hydrocarbons, but when dried yielded a dark brown solid wax

The method of examination of the extract was based on the selective action of various organic solvents The crude wax (750 grams) was therefore mixed with purified sawdust and successively extracted (24 hours for each extraction) with light petroleum, ether, benzene, alcohol and chloroform, the following separation being obtained

TABLE VIII

Material Extracted

Solvent.	Sparingly Soluble	Readily Soluble	Total Extract	Percentage of Crude Material.
Light Petroleum .	213 g	245 g	458 g	60·7 per cent.
Ether . . .	54	17·5	71 5	8 6 ,,
Benzene . .	73	9	82	12 8 ,,
Alcohol . . .	24·5	15	39 5	5·0 ,,
Chloroform . .	12	5	17	2·2 ,,

The constituents of these various extracts were shown to be .

TABLE IX

'Sparingly soluble $\begin{cases} \gamma\text{-GOSSYPYL ALCOHOL}^1 \\ \beta\text{-Gossypyl alcohol} \end{cases}$

Light petroleum extract .

'Readily soluble { 'Free acids—palmitic, stearic and *oleic*
| Acids as esters—CARNAUBIC, palmitic, stearic and oleic
Montanyl and *gossypyl* alcohols
Solid hydrocarbons — *triacontane* and *hentriacontane*
LIQUID HYDROCARBONS
Phytosterol, principally sitosterol
Amyrin

[1] α, β, and γ gossypyl alcohols have now been shown to be identical (Fargher and Probert, *Journ. Text. Inst* , 1924, xv. 337).

Ether extract . .
  Sparingly soluble { MONTANYL ALCOHOL.
  Sitosterolin
  Palmitic acid
  Stearic acid

  Readily soluble { Montanyl alcohol
  Palmitic and stearic acids.

Benzene extract . .
  Sparingly soluble   β-GOSSYPYL ALCOHOL.

  Readily soluble { *β-Gossypyl alcohol*
  Palmitic and *stearic* acids.

Alcohol extract . .
  Sparingly soluble { α-Gossypyl alcohol.
  Ceryl alcohol
  Sodium salts of montanic, cerotic, palmitic and stearic acids.

  Readily soluble { Sodium salts of fatty acids (united with similar material from sparingly soluble portion)

Chloroform extract . . . . . . { α-Gossypyl alcohol.
  Carnaubyl alcohol
  An acid

In the above table, substances present in large amount are shown in capitals , those present in very small amount in italics

Gossypyl and montanyl alcohols appear to be new substances; the acid found in the chloroform extract was shown to be $C_{34}H_{68}O_2$, and various derivatives of it were prepared, although it was not identified with any known acid

Gossypyl alcohol, $C_{30}H_{62}O$, the main constituent of the benzene extract of cotton, occurs in three forms, neither of which is identical with melissyl alcohol, $C_{30}H_{61}OH$, which is found in beeswax. These a, β and γ alcohols differ in melting-point—a, m p 87°-88° C , β, m p. 86° C., γ, m p. 82°–83° C , and in their solubilities in organic solvents, though they yield identical derivatives and the same acid on fusion with potash-lime.

Montanyl alcohol, $C_{28}H_{58}O$, m p. 85°–86° C., yielded on fusion with potash-lime, an acid which appeared identical with montanic acid—a constituent of montan wax.

The original cotton sliver was extracted in a Soxhlet apparatus for 8 hours with benzene, whereby an extract amounting to 0·47 per cent calculated on the

air dry cotton (0·51 per cent on dry cotton) was obtained, and shown to have the following characteristics

Melting-point	70–75° C.
Density	0·989
Acid value	30·6
Saponification value	65
,, ,, after acetylation .	144
Acetyl value	83
Iodine value	21
Unsaponifiable matter	51 (suspected to be somewhat low)

A specimen of Schunk's original cotton wax was examined at the same time, and shown to have m p 80°–86° C and a saponification value of 31·6 ; an acid, m p. 91° C. and an alcohol, m p. 79·5° C. were isolated from it

This excellent investigation by Fargher and Probert unfortunately had a slightly decreased value in consequence of the fact that, owing to the method of extraction, the possibility of saponification and the extraction of substances other than wax could not be avoided.

Mineral Constituents.

The mineral constituents of cotton are varied and similar to those usually found in plants. Ure (Bowman) found a sample of Sea Island cotton to contain I per cent. of ash, having the following composition

TABLE X

Mineral Constituent		Amount
Potassium carbonate . . .	44·80 per cent.
,, chloride . . .	9·90 ,,
,, sulphate . . .	9·30 ,,
Calcium phosphate . . .	9·00 ,,
,, carbonate . . .	10·60 ,,
Magnesium phosphate . . .	8·40 ,,
Iron oxide	3·00 ,,
Alumina and loss	5·00 ,,

It will be understood that the ash will be high or low according to the cleansing of the cotton. Raw cotton, straight from the bale, is liable to contain earth and sand.

It is generally true that the mineral constituents of cotton and their effect on subsequent processes of manufacture have not been thoroughly investigated. The recent work of Geake (*Journ. Text. Inst.*, 1924, xv. 81) on the phosphorus content of cotton is, therefore, of particular interest.

The determination of the phosphorus content was made (see page 211) by reducing the cotton to ash, dissolving this in sulphuric acid, precipitating the phosphorus as strychnine phosphomolybdate, separating this by centrifuging, and comparing its volume with a known amount of phosphorus precipitated in a similar manner.

Some typical results are given in the following table :

TABLE XI

Type of Cotton	Nature of Sample.	P₂O₅ Content.
American (Texas) . . .	Combed sliver.	0·042 per cent.
„ (Georgian) . .	Yarn	0·044 „
„ (Long Staple Upland) .	Combed sliver.	0·061 „
Sea Island (West Indian) .	Sliver.	0·064 „
„ „ . .	Combed sliver.	0·057 „
„ „ . .	Yarn.	0·066 „
Egyptian (Uppers)	Roving.	0·077 „
„ (Best Uppers) . .	Yarn.	0·089 „
„ (Brown Mitafifi)	Roving	0·105 „
„ (Sakellaridis) .	Sliver	0·134 „
„ „ .	Combed sliver.	0·117 „
„ „ .	Yarn	0·105 „
Indian (Surtee) . . .	Slubbing.	0·118 „
„ (Oomra) . . .	„	0 054 „
„ (Bengal Fine) . . .	„	0·071 „
South American (Peruvian Mitafifi) .	Slubbing.	0·075 „
„ (Tanguis) . .	Yarn.	0·063 „
Australian (Queensland) . . .	Sliver.	0·083 „

Owing to uneven mixing cotton taken from the bale and separated from impurities had a very irregular phosphorus content, but consistent results were obtained with cotton at any stage of manufacture (exclusive of bleaching, whereby nearly all the phosphorus is removed from cotton) subsequent to carding.

The above results show that it is possible to distinguish between certain cottons, particularly between Egyptian and American cottons, by means of their phosphorus contents   Thus American cottons have a phosphorus content of 0·04–0 06 per cent. P_2O_5, whereas Egyptian Sakellaridis cotton (90 per cent. of the present Egyptian crop is Sakellaridis) has a content of approximately 0·12 per cent P_2O_5.

Cotton grown in Arizona from Egyptian seed retained its characteristic high phosphorus content 0·105 per cent. P_2O_5

Mature cotton contains less phosphorus than immature cotton.

Purification of Cotton-Cellulose.

It is generally assumed among cotton dyers, manufacturers of artificial silks and explosives, papermakers, and in other industries in which cotton or wood cellulose is employed, that the best results are obtained with cellulose which is perfectly pure. The purification of cellulosic materials is therefore of considerable importance and in the textile industry is termed bleaching

The purification of cotton, however, introduces certain considerations which are frequently overlooked When cotton is referred to as true or normal cellulose associated with fats, waxes, coloured pigments, nitrogenous matters and mineral substances, it is generally assumed that the cellulose is not chemically combined with these substances, and that removal of these by methods calculated to avoid chemical decomposition of the cellulose will result in the production of a residual normal cellulose This assumption, though probably true, has no foundation in fact, since the exact chemical constitution of cellulose and, in particular, its molecular complexity, are unknown The cellulose which is obtained as a result of careful bleaching of cotton may therefore be looked upon as pure cellulose but not necessarily normal cellulose In all industries which utilise cellulose, pure cellulose will, therefore, be considered as a raw material which is as near an approximation to normal cellulose as it is possible to obtain.

FIG 5 —APPARATUS FOR PROCURING STANDARD PURE COTTON-CELLULOSE.

The methods for producing pure cellulose from cotton are distinctly different from those for obtaining it from cellulosic materials such as wood, straw and grasses, since the latter products contain considerable amounts of impurities such as lignin, intimately associated with the cellulose Here it is intended to deal only with the purification of cotton.

The following is the method proposed by The Cellulose Division of The American Chemical Society (*Journ. Ind Eng Chem*, 1923, xv. 748) as a standard procedure for the preparation of " a standard cotton cellulose " (pure cellulose).
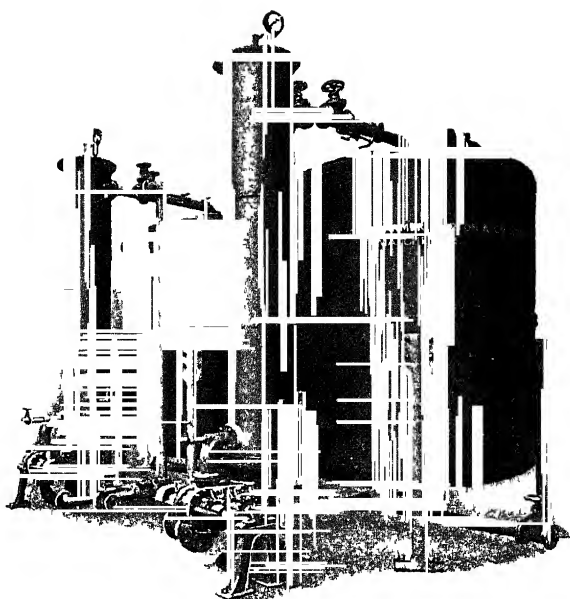
FIG 6—HIGH-PRESSURE KIERS WITH HEATERS FOR BLEACHING OF
COTTON FABRICS

(Sir J Farmer, Norton & Co Ltd)

" Mechanically clean 100 g of Wannamaker's Cleveland raw cotton by removing the seeds and other visible impurities by hand-picking. Place the cotton loosely in a nickel gauze container, to which a small nickel chain passing through the hole in the centre of the cover of the glass vessel is attached (see Fig. 5)

" Raise a rosin-soap solution containing 30 g. of sodium hydroxide and 15 g. of rosin in 3000 c.c. of water, to boiling-point, and then immerse in it the cotton within the nickel container. Boil for 4 hours, the container being mechanically subjected to a continuous vertical up and down movement, and exposure of the cotton to air avoided.

" Displace the brown alkaline solution with hot distilled water until the wash water is only slightly alkaline

" Again heat the cotton for 15 minutes with an additional 3000 c c. of caustic soda solution containing 5 g. of sodium hydroxide in 3000 c.c. of water, and afterwards remove the liquor by displacement with hot distilled water. In this manner, the rosin is largely removed

" Again treat the cotton for 10 minutes with 3 000 c.c. of boiling dilute caustic soda containing 3 g of sodium hydroxide by weight, and then displace the caustic solution by hot water. Dump the cotton from the nickel container into cold water in a large glass beaker and allow it to cool to 18°–20° C. Drain the cotton and then bleach it by immersion in 3000 c c. of a solution of sodium hypochlorite containing 0·1 per cent of available chlorine, at 20° C.

" After immersion for 1 hour in this solution in diffused light, rinse the cotton by washing on a Buchner funnel with distilled water for 10 minutes, repeating the operation three times. During the last rinsing, add a saturated solution of sodium bisulphite drop by drop until the filtrate does not colour starch iodide paper. Again rinse the cotton with distilled water and then dry by folding it in linen cloth surrounded by high-grade filter paper and subjecting to hand pressure, leaving the material for several days in a room where no fumes can affect it.

" The standard cellulose thus prepared is found to contain a very small trace of fat which is so slight as to be considered negligible, but which may be removed by solvent extraction by means of alcohol-benzene. A few results showing the effect of this process of purification are added, it being noted that normal cellulose should contain no fat, mineral substance, nitrogen and should have a copper number of 0."

TABLE XII

Raw Cotton (Wannamaker's Cleveland)

	I	II.	III.
Cellulose . . .	89 55 per cent	90 45 per cent.	89·35 per cent.
Ash	1·10 ,,	1·00 ,,	1 09 ,,
Cuticular matters .	0·71 ,,	0·69 ,,	0·72 ,,
Fats and wax . .	4·10 ,,	4 08 ,,	4·00 ,,

4

TABLE XIII

Purified Cotton (Wannamaker's Cleveland)

	I.	II	III
Cellulose . . .	99·56 per cent	99·61 per cent	99·62 per cent.
Nitrogen . . .	Nil	Nil	Nil
Fat . . .	Nil	Nil	Nil
Ash	0·09 per cent.	0·09 per cent.	0·09 per cent.
Copper number. .	0·30 ,,	0·32 ,,	0 28 ,,

The method described above for preparing standard cellulose is based on the same principles which govern the technical purification of cotton   That is, an alkali-boil is employed for the removal of fats, waxes and protein matters, while colouring matters are destroyed by means of a hypochlorite.   During technical purification, however, cotton is treated with acids, particularly after treatment with a hypochlorite ; this is avoided in the laboratory method indicated above   Mineral substances are of course removed during the numerous washings

Technical bleaching has also to effect the removal of various substances (starch sizes) which are added to cotton for the purpose of facilitating spinning and weaving.   Its severity is governed by the dyers' and finishers' requirements —whether a thorough or but a moderate bleach.

The more important methods of technical bleaching, as applied to fabrics, will now be described, but it will be understood that the same treatment is applied to cotton in yarn or loose form with slight modifications.

For the production of a perfectly pure cotton fabric, many Lancashire bleachers believe that the good old-fashioned " madder bleach " is necessary, and there is certainly not sufficient evidence to prove otherwise, though many bleachers prefer a shorter method.

In the " madder bleach," the cotton fabric is steeped in water for about 12 hours, usually after a preliminary process of singeing, whereby loose fibres projecting from the fabric are removed.   Afterwards, it is thoroughly impregnated in rope form with a ½ per cent. milk of lime suspension, carefully packed in a kier (Figs 6 and 7) and there boiled, with a comparatively small quantity of water for several hours.   The boiling usually takes place under pressure, so that the temperature is raised above 100° C., and continuous circulation of the liquor through the fabric is maintained by means of a steam injector or heater.

During this lime boil, the fats and waxes present in the cotton are converted

into calcium soaps, and nitrogenous substances are removed in the form of ammonium salts

The fabric is then removed from the kier, well washed in water and then
" soured," that is, treated
with cold acid (hydrochloric
or sulphuric) of 1°-2° Tw.
Mineral matters are thus
largely removed and the
calcium soaps are decom-
posed, leaving the free fatty
acids in the fabric

Again the fabric is
packed in the kier and sub-
jected to the first " lye
boil," an operation exactly
similar to the lime boil,
except that caustic soda or
soda ash, or a mixture of
both, together with a smaller
amount of resin, are em-
ployed instead of lime   On
removal from the kier, the
fabric is freed from sodium
soaps by washing with
water. Subsequently, the
fabric is again subjected to
a short boiling with soda
ash in the kier and is then
finally thoroughly washed
with water and some-
times again soured and
washed.

After these operations
of steeping, lime boiling and
lye boiling, the fabric is free
from practically everything
except the natural colouring
matters originally present in
the cotton, and these are
therefore removed by " chemicking "

FIG. 7.—HIGH-PRESSURE KIER WITH MULTITUBULAR
HEATER SECTIONAL VIEWS
(Sir J. Farmer Norton & Co. Ltd)

In chemicking, the fabric is impregnated with a solution of calcium or sodium
hypochlorite (usually containing 0·10-0·50 per cent of available chlorine per litre),
allowed to lie in a pile for a few hours, is then washed with water, soured with

1-2 Tw hydrochloric acid, and again thoroughly washed with water, mangled and dried. In some instances, the fabric is treated with an antichlor such as a solution of sodium bisulphite or thiosulphate before being finally washed.

A less drastic bleach is obtained by means of the *soda boil*. No lime or resin is used in this process, the fabric, after steeping, being boiled in a kier, generally under pressure, with a 2 per cent solution of caustic soda or sodium carbonate, and afterwards washed and bleached to white by chemicking. Often two soda boils are carried out, the fabric being washed with water after the first. This method of bleaching yields a pure fabric and is largely employed.

For several years the possibilities of solvent extraction as an aid or as a substitute for the usual methods of bleaching have been discussed, and from a theoretical standpoint the use of organic solvents for the removal of the fats and waxes from cotton seems ideal. In practice, however, the loss of a costly solvent, in spi te of recovery processes, and the attending risks of fire, have to be considered   At present, solvent extraction has not been generally adopted. Fort (*Journ Soc. Dyers & Col*, 1921, xxxvii. 162 ; 1923, xxxix 42), however, gives a restricted description of the working of a large plant at Perth which has been erected for the solvent extraction of cotton and linen (see also E P. 165198/20 and 170534/21).

From experience, Fort indicates that solvent extraction cannot be considered as a substitute for ordinary bleaching processes but only as an adjunct. For instance, in cases where fabrics containing coloured effects have to be bleached, previous solvent extraction enables good whites to be obtained with a comparatively mild bleaching treatment, and the colour bleeding which could not be prevented during the more usual and drastic method of bleaching is thus avoided.

In certain instances, successful beetle finishes are dependent on the perfect freedom of the fabric from fat or wax ; solvent extraction allows this condition to be obtained

The solvent extraction of wool is carried out with low boiling solvents such as petrol, but cotton appears to be more amenable to extraction with heavier solvents such as benzene and toluene   In this case, wet fabric may be subjected to the vapours of the solvent until all the moisture is displaced, and the extraction proper by means of the solvent may then be effected. Subsequently the solvent may be displaced by steam   Such a cycle of operations is readily carried out so that the solvent may be recovered

In no instance has it been proved that the wax recovered as a by-product meets the cost of the extraction to an extent which would encourage the installation of the necessary plant for this reason alone. Generally, it may be inferred that at the present time solvent extraction is more costly than ordinary methods of bleaching   It should be remembered, however, that solvent extraction is very largely carried out in the dry cleaning and dyeing trade.

The full bleaching of cotton is long and tedious, but as yet no successful short cuts are possible. Kier boiling of one kind or other appears to be essential, and
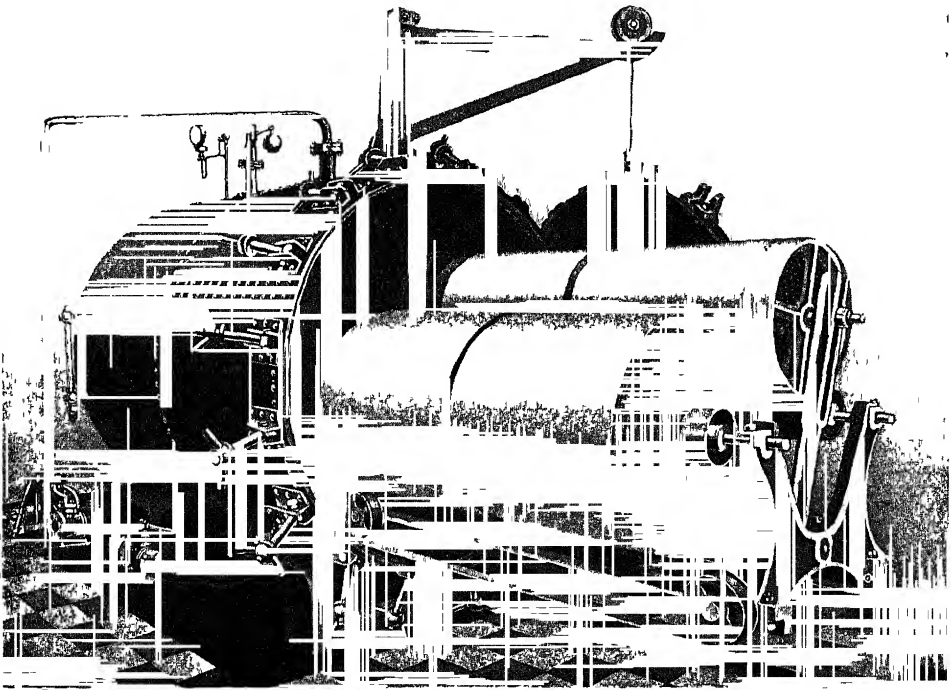
FIG 8 —PATENT OPEN WIDTH BLEACHING KEIR
(Jackson & Brother Ltd)

unsatisfactory results are obtained when grey fabric is chemicked directly. For instance, one process, stated to have been worked on full scale and in which grey fabric was padded (impregnated) with caustic soda and then passed through a chamber containing chlorine gas, resulted in white fabric which the author found to contain a considerable amount of fat and to have a high copper number, thereby indicating partial degradation of the cotton. Consequently, improvements in bleaching have been made mostly in connection with the necessary machinery. Most fabric is bleached in rope form, but in the latest methods open width bleaching (Figs. 8 and 9) is possible. In this connection, a thorough historical account of the development of bleaching has been given by Higgins (*Journ. Text. Inst.*, 1923, xiv. 209, etc.)

At times, bleaching may be more conveniently carried out by means of a
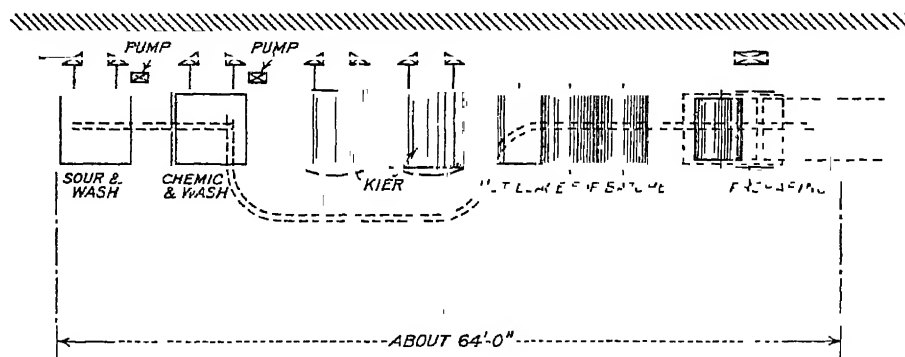
FIG. 9.—GENERAL OUTLAY OF PLANT FOR BLEACHING FABRIC IN OPEN WIDTH.
(Jackson & Brother Ltd.)

liquor containing sulphuric acid and potassium permanganate instead of a hypochlorite, but such a method is only carried out to a comparatively small extent. After the treatment with permanganate, the fabric is washed, steeped in a solution of sodium bisulphite or hydrogen peroxide whereby the brown deposit of manganese oxide is removed, and again washed and dried.

In the earliest times, water containing chlorine was used for bleaching. Subsequently the use of bleaching powder was developed; then solutions of sodium hypochlorite, bought as such or prepared at the bleach works by electrolysis of aqueous solutions of salt, were introduced and these are now largely used. More recently, with the availability of compressed chlorine, there is a tendency to revert to the use of chlorine water or solutions of hypochlorite prepared at bleach works from chlorine gas.

Persistent endeavours are also being made to utilise the bleaching properties of hydrogen peroxide and related products. Their expense prevents their use for ordinary bleaching of fabrics, but hydrogen peroxide is largely used in the bleaching of cotton and artificial knitted goods.

Useful information concerning the use of hydrogen peroxide in bleaching is given by Weber (*Journ Soc Dyers & Col*, 1923, xxxix. 209). The commercial product is usually of 12-volume strength and contains a small amount of acid to render it stable during storage. Metals such as iron and copper catalytically effect the rapid decomposition of hydrogen peroxide, but nickel (E.P 188811/21) does not and may therefore be used in the construction of bleaching plant. Wood disintegrates when exposed to the prolonged action of hydrogen peroxide, and lead is oxidised to lead peroxide, so that the bleaching plant should be constructed of enamelled iron or glazed bricks Lead or preferably tin heating coils are serviceable

The actual bleaching is effected with a liquor prepared by adding 40 gallons of 12-volume hydrogen peroxide to 240 gallons of water containing 2 lb of sodium silicate whereby the mixture is slightly alkaline to litmus Previously scoured cotton is immersed in this for 5–10 hours at 40°–50° C. and is then washed, a good white being thus obtained

As previously indicated, it is essential that the purification of cotton by the above methods should be effected with the minimum of modification or degradation of the cellulose Cotton is not appreciably degraded by treatment with alkalis in the absence of oxygen, but when air or oxygen is also present, the cellulose is easily oxidised. Degradation of the cellulose also easily occurs when cotton is in contact with acids or oxidising agents (chemic), and this leads (see later chapters) to considerable modification of the physical and dyeing properties of the cotton.

The progress of purification may be followed by chemical examination of the cotton for its content of mineral and organic impurities. In technical practice, however, there is no opportunity for this prolonged investigation, and the degree of purification is usually judged by the resulting purity and permanence of the resulting white. It is very probable that mineral and nitrogenous substances are largely removed early in the purification process, and Knecht and Hall (*Journ Soc. Dyers & Col.*, 1918, xxxiv 220) support this by the following results

TABLE XIV

Treatments Effected Successively.	Residual Nitrogen
Lime boil	54 0 per cent. of original N content
Sour with HCl	40 5 　　,,　　　,,　　　,,
NaOH boil	27 1 　　,,　　　,,　　　,,
Sour with HCl .	16 8 　　,,　　　,,　　　,,
Chemic	6 7 　　,,　　　,,　　　,,
Sour with HCl	5 8 　　,,　　　,,　　　,,

Higgins (*Journ. Soc. Dyers & Col*, 1919, xxxv. 164) has also observed that after the first alkali boil, about 91·5 per cent of the original content of nitrogen is removed

Recently, however, physical methods have been improved so that the progress of purification can be followed more readily. It is found, for instance, that a 2 per cent solution of raw cotton in cuprammonium solution has a very high viscosity, while degraded cotton, under similar conditions, possesses but a low viscosity Mechanical damage to cotton has, of course, no effect on this viscosity, so that a means is therefore available for determining the severity of the purification treatment. This is further dealt with in Chapter V, and the effects of technical purification on the viscosity of cotton discussed.

It is also found that impure cotton has a comparatively high absorptive capacity for Methylene Blue, and that this may be employed as an approximate measure of the progress of purification. Investigations of Birtwell, Clibbens and Ridge (*Journ Text Inst*, 1923, xiv. 227) indicate that this absorption is partly dependent on the alkalinity of the ash, the origin of growth and the pectic impurities of the cotton, but that when allowance is made for the ash and origin of the cotton and the possibility of its attack by oxidising agents is excluded, the absorption is a measure of the efficiency of bleaching.

The following results were obtained as showing the progressive fall in the absorption of Methylene Blue which accompanies the purification of American cotton in the form of fabric

TABLE XV

Treatment	Methylene Blue Absorption Millimoles per 100 g of Dry Cotton
Grey fabric	2 16
Lime boiled and soured	1·58
,, ,, and ash boiled . . .	1·04
,, ,, ,, ,, and chemicked	1 04
Lime boiled and soured and ash boiled and chemicked and ash scalded	0·58
Lime boiled, soured, ash boiled, chemicked, ash scalded and chemicked	0·57

Some further results, given below, indicate that solvent extraction does not appreciably affect the absorption of Methylene Blue

TABLE XVI

Treatment.	Methylene Blue Absorption. Millimoles per 100 g of Dry Cotton
Unbleached sliver	4·05
,, ,, extracted for 6 hours with petroleum	4·11
,, ,, extracted with chloroform . .	4 10
Sliver spun into yarn, kier boiled and acid washed .	0·57

CHAPTER III

COTTON AND ALKALIS

SINCE 1844, when John Mercer noticed that caustic exerted a profound change on the chemical and physical properties of cotton, the action of alkalis on cotton has become a subject of much importance. The ever-increasing amount of literature relating to this subject is evidence of its strong appeal to textile chemists.

Mercer observed that when cotton was steeped in a strong solution of caustic soda, the fibres swelled and shrunk in length. After removal of the alkali by washing with water or by treatment with acid, the resulting cotton had an increased absorptive power for dyestuffs.

Subsequently Lowe noticed in 1889, that if cotton treated with caustic soda was maintained in a stretched condition during the removal of the alkali by washing, the resulting cotton had an increased lustre

Nearly all investigations concerning the behaviour of cotton towards alkalis have been directed towards the elucidation of these two fundamental discoveries of Mercer and Lowe

Cotton and Caustic Soda.

In the first place, it should be noted that cotton is affected by caustic soda of all strengths, but only under conditions of fusion at high temperatures (approaching 200° C.) does the cotton suffer disintegration into simpler and more soluble products The progressive nature of the action of caustic soda on cotton was first clearly demonstrated by Pope and Huebner (*Journ Soc. Chem Ind.*, 1904, xxiii 404), the action being evident by the shrinkage produced. In the following table is given the results obtained by immersing skeins of cotton yarn, each of 200 yards in length, for 30 minutes in cold solutions of caustic soda of varying concentrations, the resulting length of the yarn being measured while it was still saturated with the alkali.

Subsequently, the hanks of yarn treated as above were dyed under standard conditions with 0·25 per cent of Benzopurpurine 4B, and the resulting shades compared The results appear (see page 75) to more or less agree with the measurements of shrinkage—that is, greater dyeing capacity coincides with greater shrinkage.

Later, Knecht (*Journ Soc Dyers & Col.*, 1908, xxiv. 67) further showed (see page 74) the progressive action of caustic soda on cotton yarn by quantitative measurement of the dyeing capacity of cotton mercerised with increasing strengths of caustic soda

Experiments on mercerisation carried out with cotton in the form of yarn can give only information which is limited , the changes which occur in the individual fibres are partly masked by slip and rearrangement among them-

TABLE XVII

Strength of Caustic Soda	Length of Hank after Treatment.	Strength of Caustic Soda.	Length of Hank after Treatment
	200 yards	22° Tw	171 3 yards.
0° Tw.	198·0 ,,	24°	163·1 ,,
1°	196·4 ,,	26°	160 3 ,,
2°	195·7 ,,	28°	160·0 ,,
3°	195·6 ,,	30°	158·2 ,,
4°	195·5 ,,	35°	150·2 ,,
5°	195·2 ,,	40°	143·7 ,,
6°	194·2 ,,	45°	141·0 ,,
7°	193 7 ,,	50°	142 2 ,,
8°	194·2 ,,	55°	142 7 ,,
9°	194·0 ,,	60°	145·3 ,,
10°	194·2 ,,	65°	149 2 ,,
12°	194·5 ,,	70°	150·3 ,,
14°	192·7 ,,	75°	152 8 ,,
16°	190·4 ,,	80°	154·2 ,,
18°	188·7 ,,	..	..
20°	186·8 ,,	..	..

selves Moreover, imperfect penetration of the yarn by the alkaline liquor, a feature of industrial mercerisation, is possible, and the results will be influenced to that extent.   Later research has therefore been directed to the behaviour of single cotton hairs during mercerisation.

Willows, Barratt and Parker (*Journ Text. Inst*, 1922, xii 229) describe the changes in length, and Willows and Alexander (*ibid*, 237) the changes in cross-section of single hairs of scoured Egyptian sliver

In these experiments, single cotton hairs were maintained taut between clips, under a load of 50 mgs , during their treatment with solutions of caustic soda.   Since the breaking strain of such hairs was 6–7 g., it can be considered that they were thus nearly free from tension   The changes produced during mercerisation were found to be complete within about 3 minutes (see Fig 10) and with solutions of 25°–45° Tw the changes were 75 per cent complete during the first half-minute.

Single cotton hairs were therefore mercerised for 3 minutes and then washed in cold water, the changes in length being observed on the wet hairs immediately after mercerisation and after washing.   The results show some striking differences from those obtained by Pope and Huebner on yarn (see Fig 11).

Willows, Barratt and Parker direct attention to the following interesting features

1 Fibres have their maximum length when in lye of 10° Tw.   The change of length is probably due to the gradual softening of the fibres and the straightening

out of the convolutions, as a similar extension, but less in amount, occurs in water

2 The big change beginning shortly after 20° Tw. That mercerisation rapidly sets in about 22° Tw has been independently noticed by Wigley, who observed that when scoured sliver is immersed in caustic soda of 20° Tw., the colour is scarcely changed and the cotton appears as bright as it does in water When caustic soda of 23° Tw is used, the cotton becomes darker, duller and slimy Also, hairs treated on the microscope stage with 20° and 25° Tw solutions differ in that with the former few of the convolutions are removed, but with the latter most of them disappear, although the fibre outline is still irregular

3 The marked contraction at 30° Tw Structural changes have also been noticed here.

4 Of solutions between 25° and 68° Tw , that at 40° Tw. brings about the minimum contraction. Hence, if it be required to print NaOH on a fabric so as to produce a greater affinity for dyes and but little shrinkage, 40° Tw. should be used

5 The change of length produced by washing When a solution of any strength of caustic soda up to 52° Tw is washed out of cotton hairs, they extend in length ; with stronger solutions there is a contraction additional

FIG. 10 —CHANGES IN LENGTH WITH TIME OF COTTON HAIRS (SCOURED) IN CAUSTIC SODA SOLUTIONS UNDER TENSION OF 50 MG.
(Willows, Barratt and Parker)

to that produced by the alkali. If contraction be a measure of mercerisation, as is generally assumed, we may say that when such strong solutions are washed out, additional mercerisation is produced, and this effect is greater as the original solution is stronger. Thus 86° Tw. caustic soda produces practically no effect, but after washing, there is a contraction of 2 per cent

The effect of temperature upon mercerisation was not fully investigated, but a decrease of temperature causes a greater contraction above 22° Tw , and

the maximum effect is produced with weaker solutions.   For example, at 0° C. the maximum contraction is produced by a 25° Tw. solution.

An interesting feature of these investigations was that they confirmed the general observation in large scale mercerisation, that the force required to prevent yarn from contracting during mercerisation is considerably less than that
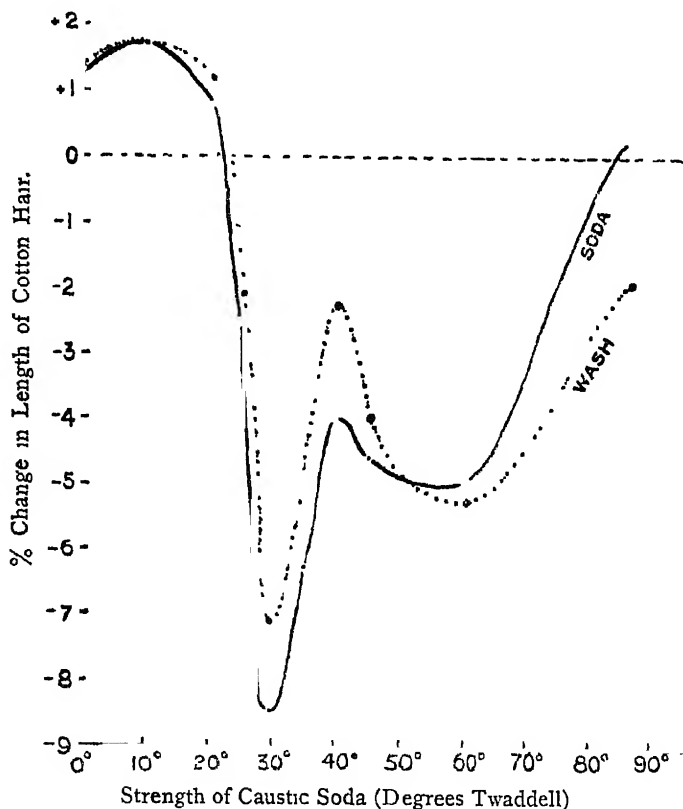
FIG. 11 —CHANGES IN LENGTH OF COTTON HAIRS (SCOURED) IN CAUSTIC SODA
SOLUTIONS UNDER A TENSION OF 50 MG.
(Willows, Barratt and Parker)

required to stretch it to its original length after having been allowed to contract freely.   Thus, when cotton hairs were immersed in caustic soda of 35° Tw no contraction occurred under a load of 0·16 g ; when allowed to contract, a force of 0·32 g was required to stretch them to their original length

After solvent extraction cotton fibres appear to suffer greater shrinkage during mercerisation

No less interesting are the changes produced in the cross-section of cotton hairs during mercerisation.

In the experiments of Willows and Alexander sections of scoured fibres (see page 221) were fixed on glass slides laid on a microscope stage illuminated with a Pointolite lamp. The eye-piece of the vertical microscope was replaced by a

Change in Sectional Area of Fibres
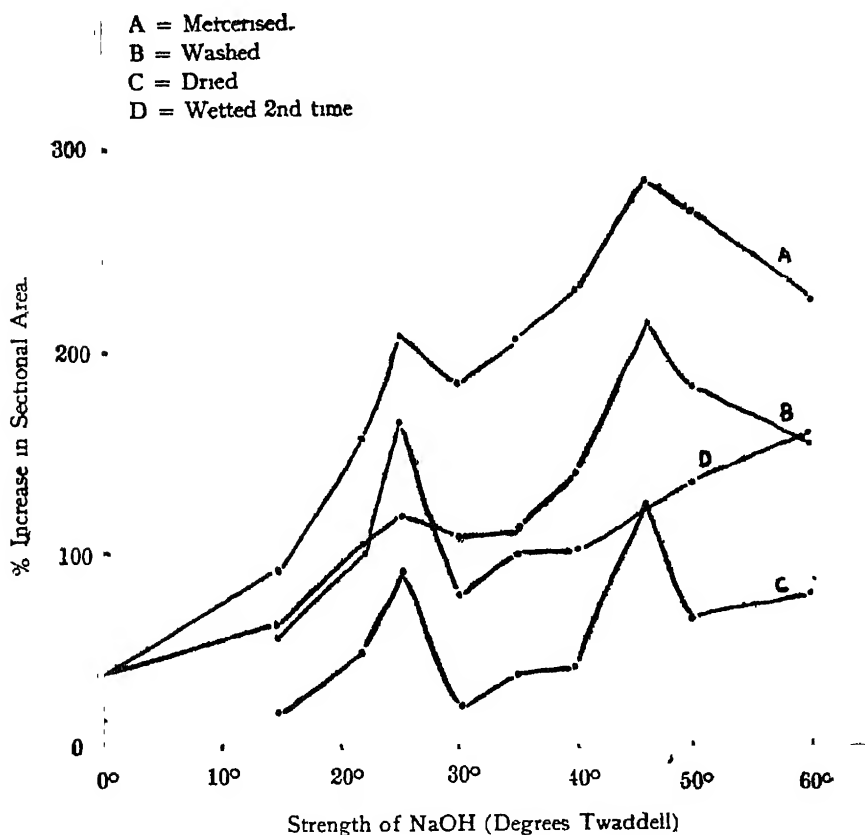
FIG. 12.—CHANGE IN SECTIONAL AREA OF COTTON HAIRS IN CAUSTIC SODA SOLUTIONS
(Willows and Alexander.)

right-angled glass prism, and an image of the section was projected on a screen at a distance of about 3 metres, thus giving a magnification of about 700 diameters It was thus possible to trace outlines, on sheets of uniform paper pinned to the screen, of cotton hairs while being treated with caustic soda or other liquors on the glass slide. The cross-sectional area of a hair could be accurately determined by weighing the area of paper covered by its image on the screen.

In the first place, it was found that when sections of cotton hairs were wetted out with water, their area increased by 40-42 per cent., and the accuracy of this measurement was within 5 per cent. The expansion of different hairs was found, however, to vary by over 100 per cent , and it was finally concluded
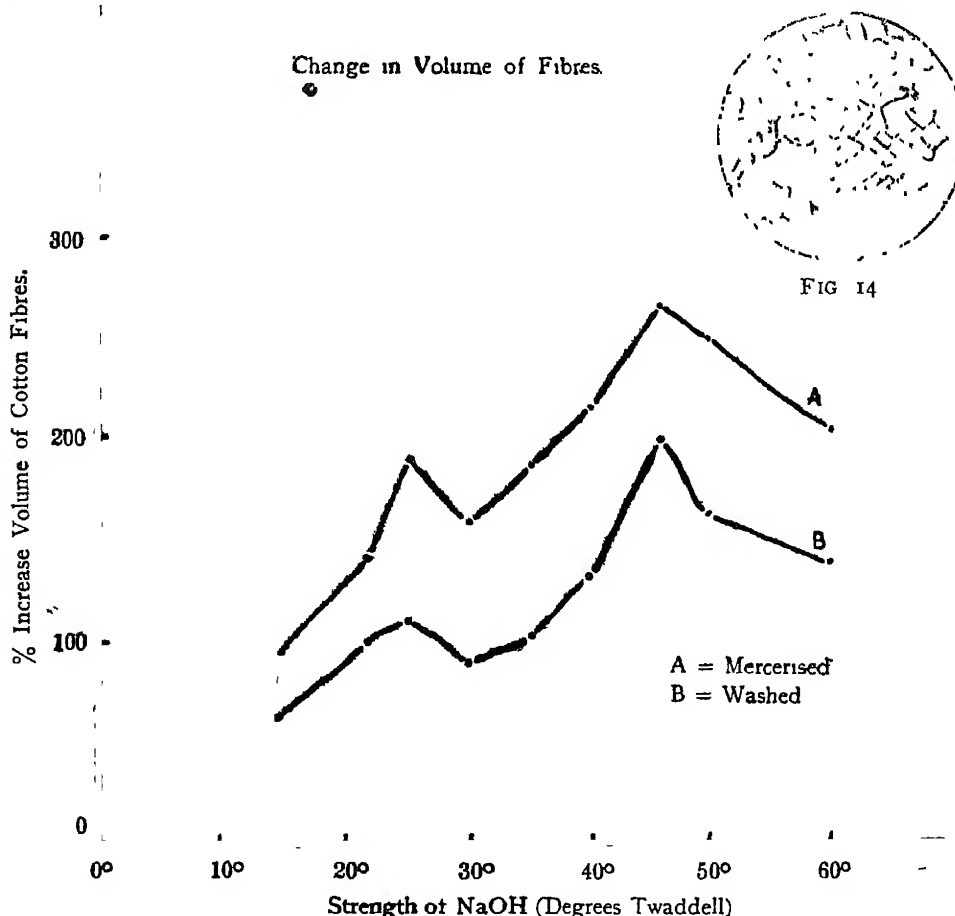
FIG. 13.—CHANGE OF VOLUME OF COTTON HAIRS IN CAUSTIC SODA SOLUTIONS
(Willows and Alexander.)
FIG. 14 —SWELLING OF COTTON HAIR SECTIONS IN CAUSTIC SODA SOLUTIONS
(Willows and Alexander)

that these differences were not errors of experiment, but were due to differences in the behaviour of the hairs

The results are shown in Fig 12 and indicate the change in cross-sectional area when a cotton hair is mercerised, then washed with water, afterwards dried and again wetted out with water. Actually some hundreds of cotton hairs were employed in the determination of each point on the curves.

From the changes in length previously obtained by Willows, Barratt and Parker, the changes in volume of cotton hairs under these treatments were calculated and are shown graphically in Fig. 13.

The process of mercerisation is thus shown to be very complex, and the results indicate that the auxiliary processes of washing with water and drying play a not inconsiderable part. The changes in length and sectional area appear
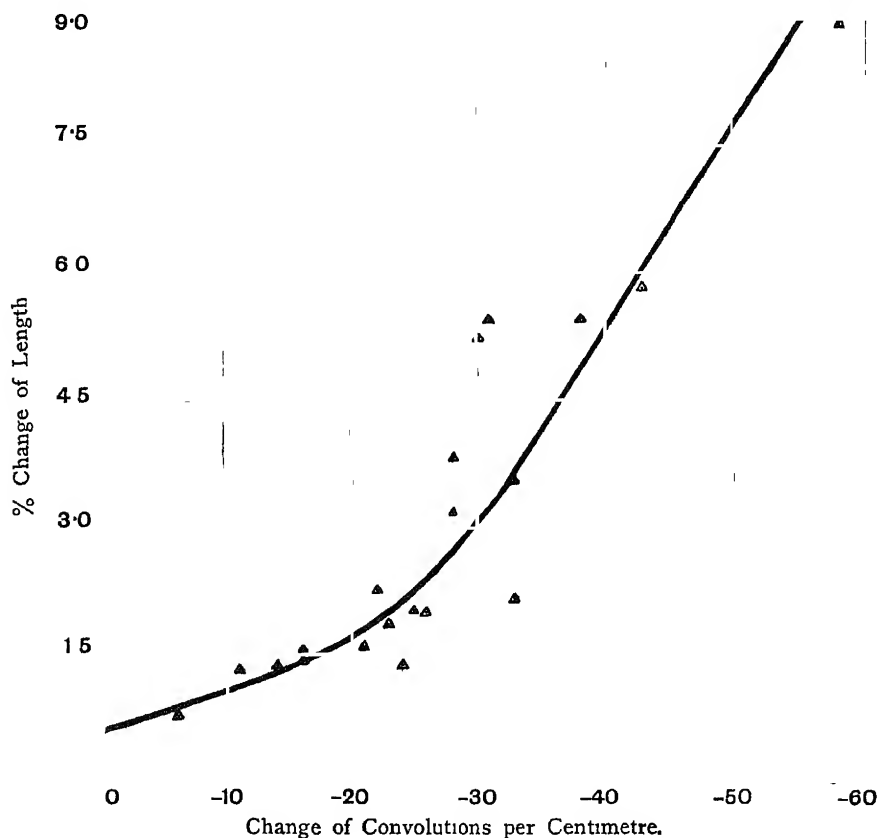
FIG 15.—CHANGE IN LENGTH OF COTTON HAIRS IN DISTILLED WATER
WITH CHANGE IN NUMBER OF CONVOLUTIONS PER CM.
(Collins and Williams.)

to be approximately greatest with a mercerising liquor of 30° Tw. A further interesting feature was observed when sections were mercerised with liquors not weaker than 25° Tw., or stronger than 45° Tw., and preferably of 30°–40° Tw. Under such conditions, each section took the shape of a dumb-bell (Fig 14), the cuticle apparently being subject to internal expansive forces which were able to cause extrusion of cellulose at both ends. This remarkable evidence of a protective cuticle was further confirmed by the discovery that tendered hairs, in

which the cuticle would be presumably weakened or destroyed, failed to develop the dumb-bell appearance under suitable conditions of mercerisation

These valuable researches on mercerisation, carried out as they were in the Research Dept. of Tootal Broadhurst Lee Co. Ltd , show how industrial science may benefit when business interests recognise their dependence on scientific research.
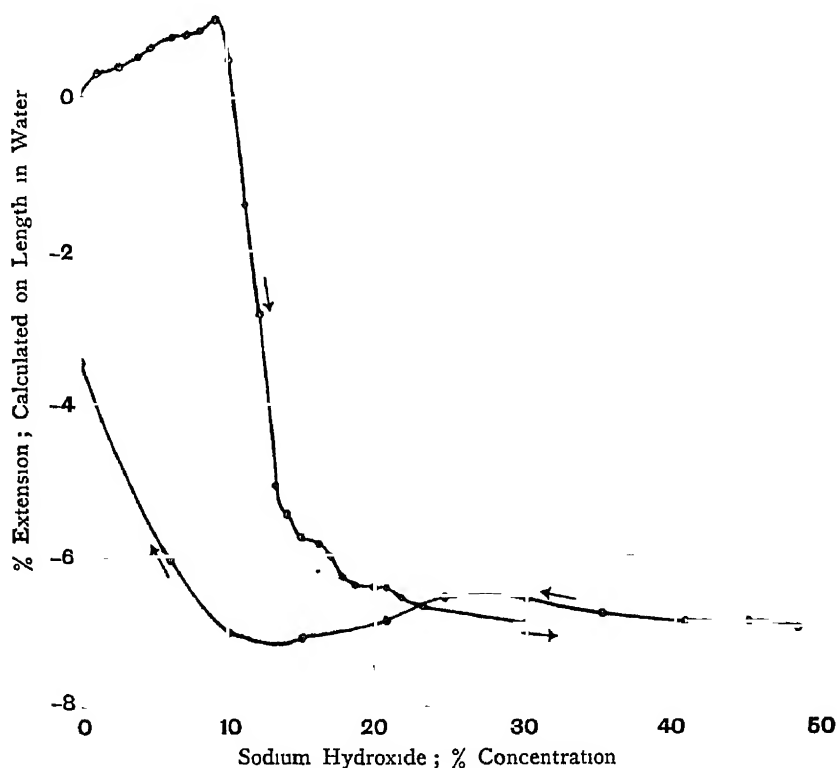
FIG 16—CHANGES IN LENGTH OF COTTON HAIRS IN CAUSTIC SODA SOLUTIONS
(Collins and Williams)

The behaviour of cotton hairs during mercerisation has also been studied by Collins and Williams (*Journ. Text. Inst*, 1923, xiv. 287), using an instrument designed on the lines of Justin-Mueller's turgometer. Both changes of length and mean diameter of the cotton hairs were measured

In the first instance, it was observed that when immersed in water or dilute solutions, cotton hairs untwisted, the number of convolutions being thus reduced and the length increased The changes in length due to this effect when cotton hairs were transferred from air of ordinary humidity (50–60 per cent.) to

distilled water, are shown in Fig 15. By the same treatment, it is observed that the mean diameter of a cotton hair increases by 7 per cent. The small real extension in length which occurs during wetting-out, as suggested by the shape of the curve in Fig. 15, is therefore exceptional, since an increase in the diameter of a cotton hair is usually associated with a decrease in length.

The results obtained are shown partly in the following table, and Fig. 16 illustrates the change in length which a cotton hair suffers when immersed in a solution of caustic soda, the strength of which is gradually increased and then reduced It is evident that the process is not reversible. The changes in length are calculated on the length of the hairs in distilled water.

TABLE XVIII

Strength of Caustic Soda		Contraction	
32°·0 Tw or	14·2 per cent	5 48 per cent.	
34° 3	15·2 ,,	5·75 ,,	
36° 6	16·2 ,,	5 86 ,,	
38°·8	17·1 ,,	6 00 ,,	
40° 6	18 0 ,,	6·30 ,,	
42°·8	18 9 ,,	6 36 ,,	
44°·6	19 8 ,,	6·40 ,,	
48°·2	21 4 ,,	6 54 ,,	
51°·2	23 0 ,,	6 66 ,,	
66° 5	30·0 ,,	6·88 ,,	
104°·2	48·2 ,,	6 94 ,,	

The experiments were carried out on Trinidad Native cotton and under a load of 10 mgm They confirm the initial extension of length noticed by Willows, Barratt and Parker, but not the extension noted by these investigators with solutions more concentrated than 30° Tw. (13·1 per cent.). Collins and Williams confirmed this difference by showing that cotton hairs treated with distilled water, 15·2 and 35·1 per cent caustic soda and water successively, or with water, 15 2 per cent caustic soda, water, 35·1 per cent caustic soda and water successively, contract more than hairs which are treated with either 15·2 per cent. or 35·1 per cent caustic soda alone.

Further, Collins and Williams note the existence of steps in the curve at 40° Tw , 46°–50° Tw and 81° Tw (17·5 per cent., 21–23 per cent. and 37 per cent of caustic soda).

Fig. 17 shows the relation between the average changes in length, L, mean diameter, D, and $LD^2/4$ (an approximation to the volume of the cotton hair) of cotton hairs during mercerisation with increasing strengths of caustic soda and the corresponding values when immersed in water only. Maximum swelling

5

appears to occur in caustic soda of 14·5 per cent , but it is noticeable that with increasing strength of caustic soda from about 15° Tw , contraction in the length of a cotton hair is not accompanied by an increase in diameter ; with lower strengths of caustic soda, a decrease in length appears to indicate a corresponding increase in diameter.
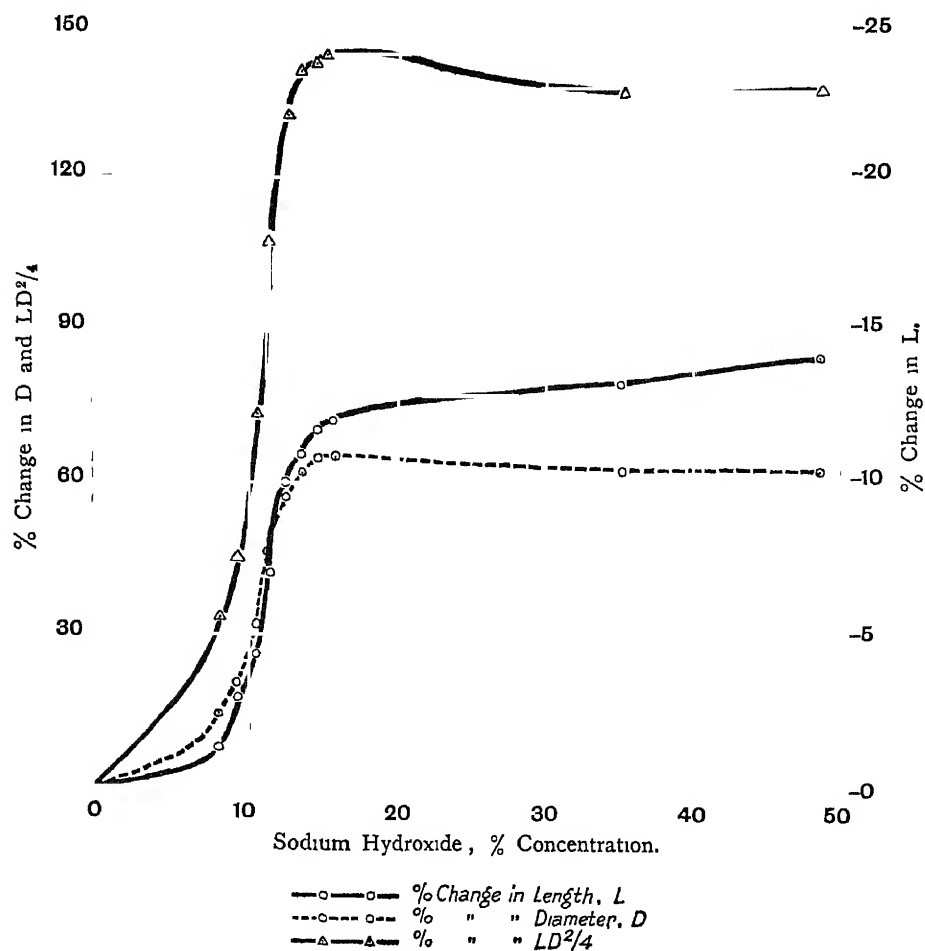
FIG. 17.—CHANGES IN LENGTH, DIAMETER AND VOLUME OF COTTON HAIRS
IN CAUSTIC SODA SOLUTIONS
(Collins and Williams)

The relationship between changes in mean length and diameter of cotton hairs during treatment with caustic soda is shown in Fig 18.   It will be seen that the mean diameter increases about five times as fast as the length decreases

Generally, it is apparent that mercerisation is practically most complete

after treatment with caustic soda of 15 per cent. (34° Tw.). The results of Willows, Barratt and Parker closely agree with this.

Evidence relating to the swelling of cotton hairs during treatment with caustic soda has been obtained by Coward and Spencer (*Journ Text Inst.*, 1923, xiv. 32) by entirely different methods Samples of Egyptian sliver scoured
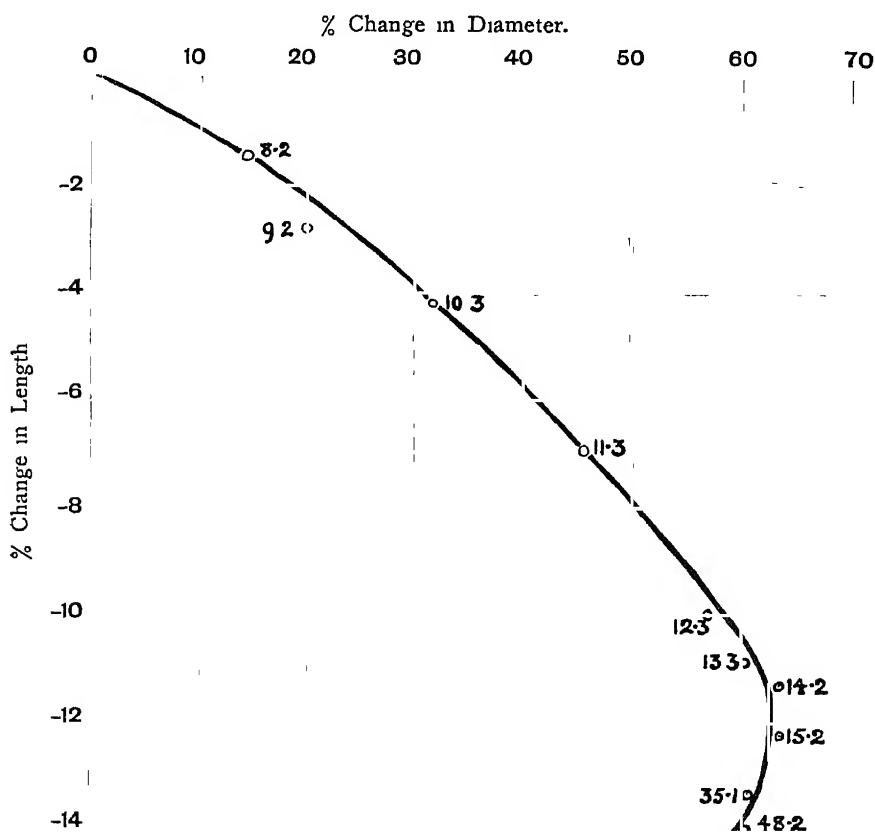
The figures by the points refer to the Concentrations % of Sodium Hydroxide.

FIG 18 —RELATION BETWEEN MEAN DIAMETER AND LENGTH OF COTTON HAIRS IN CAUSTIC SODA SOLUTIONS.

(Collins and Williams.)

with 2 per cent. caustic soda at 20 lb. pressure for 6 hours were immersed, after washing and drying at 100° C, in various strengths of caustic soda, then centrifuged to remove interfibrillar liquid (see page 84), and the amounts of sodium hydroxide and water removed by the cotton were then calculated from determinations of the weight of the dry cotton, the weight of the centrifuged mass and its content of alkali.

From the amounts of sodium hydroxide and water thus retained by the cotton, it was possible to calculate the volume which this alkali and water would occupy as a solution under normal conditions. The following results were obtained in this manner for loose cotton and also for fabric ·

TABLE XIX

Mercerising Liquor.	Calculated Volume of Caustic Soda Solution within 100 g of Mercerised Cotton	
	Loose Cotton	Fabric
0·0 g. NaOH per 100 g. of solution	52·3 c c	52 7 c c.
4·0 ,, ,, ,,	67·4	66·0
7·4 ,, ,, ,,	88 6	77·0
9·4 ,, ,, ,,	116	81
11 9 ,, ,, ,,	151	89
14·3 ,, ,, ,,	183	91
20·1 ,, ,, ,,	173	92
24 4 ,, ,, ,,	180	92
29 3 ,, ,, ,,	171	96
39 0 ,, ,, ,,	169	94
48·8 ,, ,, ,,	(184)	(99)

It was observed that the hairs of the mercerised fabric were well penetrated by the alkaline liquor, so that the less absorption of liquor by the fabric must be ascribed to the compression to which individual hairs are normally subject when in the form of yarn and fabric.

Similarly, these investigators reasonably assume that the volume of the absorbed liquor closely approximates to the degree of swelling of cotton hairs when immersed in caustic soda. They therefore compare the swelling of cotton hairs in loose and fabric form in Fig 19 and also the swelling of loose cotton, as thus obtained, with that measured by Willows and Alexander (see page 54) in Fig 20.

The lower curve in Fig 20 is due to Willows and Alexander, and, though this roughly agrees in form with the upper one, due to Coward and Spencer, there are definite differences which are probably due to the different methods of measurement employed.

FIG 19 — VOLUME OF LIQUID ABSORBED BY COTTON HAIRS IN LOOSE AND FABRIC FORM

(Coward & Spencer)

Another interesting feature which is clearly indicated by both curves in Fig 17 is that the volume of a cotton hair increases only as the strength of the mercerising liquor increases to about 14·3 per cent.; beyond that, but little further swelling takes place. This suggests that the degree of extensibility of the cuticle of a cotton hair is limited —a suggestion which agrees with the observations of Huebner and Pope (see page 70), who noticed a large number of burst hairs during mercerisation with highly concentrated solutions of caustic soda

Cotton and Caustic Potash.

Interesting results are obtained by comparison of the mercerising action of caustic potash on cotton with that of caustic soda. In technical practice, caustic potash is not employed on account of its higher cost, and this probably accounts for the fact that there is little published information relating to the action of this alkali on cellulose.

200

150

100

50

0   10   20   30   40   50

Concentration of Solution (grams of NaOH per 100 grams of Solution)

FIG. 20 —VOLUME OF LIQUID ABSORBED AND SWELLING BY COTTON IN CAUSTIC SODA SOLUTIONS

(Coward and Spencer: Willows and Alexander.)

Ristenpart (*Textilber.*, 1921, ii. 130) has, however, compared the actions of caustic soda and potash on scoured 30's double cotton yarn. This yarn was immersed, without tension, for 5 minutes in the alkaline liquor, then mangled, washed three times in much water, steeped overnight in water, then acidified with acetic acid, washed and air dried The various characteristics of the yarns were then determined, with the following results :

TABLE XX

Alkali.	Strength of Alkali	Contraction in Length.	Breaking Strain.	Elasticity	Lange [1] Time.
Untreated yarn . .		.	702 g.	7 6 per cent.	8 minutes.
NaOH	94° Tw.	37·7 per cent.	718 g	8·9 per cent.	64 minutes.
	77°	37·0 ,,	927	21·9 ,,	46 ,,
	53°	30·0 ,,	976	13 0 ,,	44 ,,
	32°	24·6 ,,	975	17·0 ,,	69 ,,
KOH	94°	33 8 per cent.	1077 g	21·4 per cent	51 minutes.
	77°	26 2 ,,	1045	14·4 ,,	41 ,,
	53°	23 1 ,,	980	15·5 ,,	57 ,,
	32°	13 8 ,,	901	11·6 ,,	50 ,,

[1] See page 88
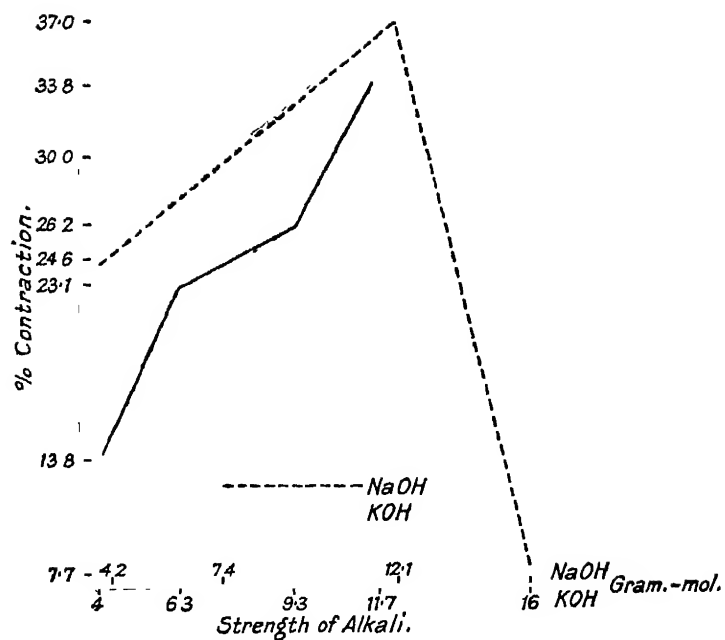
FIG 21.—CHANGE IN LENGTH OF COTTON YARN IN SOLUTIONS OF CAUSTIC
SODA AND POTASH.
(Ristenpart)
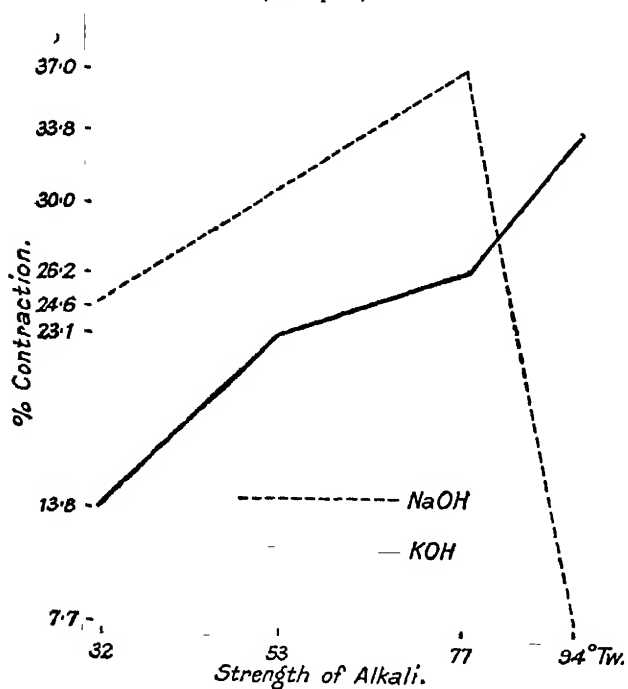
FIG. 22 —CHANGE IN LENGTH OF COTTON YARN IN SOLUTIONS OF CAUSTIC
SODA AND POTASH.
(Ristenpart)

These results are better compared by means of Figs 21 and 22. It is evident, especially when the higher molecular weight of caustic potash is considered, that caustic soda is cheaper and more efficient as a mercerising agent. Ristenpart concluded that 1 mol. of caustic soda has the same mercerising action as 1·5 mols. of caustic potash

Later investigations of Knecht and Harrison (*Journ Soc. Dyers & Col*, 1912, xxviii 224) have also dealt with the comparative action of various alkalis on cotton. Their procedure consisted of immersing two skeins of bleached cotton yarn in an alkaline solution for 5 minutes, afterwards thoroughly washing in water and drying The yarn was then measured under a tension of 1 kg Their results obtained with sodium, potassium and lithium hydroxides are given thus :

TABLE XXI

Strength of Alkali Solution	NaOH Shrinkage	Strength of Alkali Solution	KOH Shrinkage	LiOH Shrinkage
0°·0 Tw	0·00 per cent	0 0 Tw	0 00 per cent	0 00 per cent.
9°·0	0·00 ,,	8 0	0 00 ,,	0 70 ,,
13°·0	0 16 ,,	12 5	0·00 ,,	1·85 ,,
17° 0	0 47 ,,	17 0	0 31 ,,	1 5 ,,
21°·0	1 72 ,,	21 0	0 95 ,,	1·75 ,,
24° 5	2 50 ,,	25·0	2·81 ,,	2·94 ,,
24° 5–80° C	0 50 ,,	··	··	··
28° 0	4 15 ,,	29 0	5·16 ,,	··
31° 0	8 60 ,,	33·5	8 21 ,,	··
34° 5	13·05 ,,	38 0	11·55 ,,	··
38°·0	17·50 ,,	42 0	16·90 ,,	··
41°·0	23 60 ,,	46·0	17 90 ,,	··
44°·0	23 80 ,,	50·0	18·80 ,,	··
47°·0	24 20 ,,	54·0	20·30 ,,	··
50°·0	23 80 ,,	58 0	21 70 ,,	··
52°·5	22 80 ,,	62·0	22·60 ,,	··
55°·0	22·60 ,,	66·0	22 80 ,,	··
55° 0–80° C	16·7 ,,	··	··	··
·	·	81 0	23 20 ,,	··
·	·	89·0	23·40 ,,	··
·	··	95 0	23·70 ,,	··
·		102·0	24·40 ,,	··
95°·0	18 15 ,,	109 0	25·00 ,,	··
95°·0–80° C	22·80 ,,	116 0	25·70 ,,	··
		123 0	22 60 ,,	··

These results are also expressed in Fig. 23, and it is again seen that yarn apparently does not extend in length when immersed in weak solutions of caustic alkali

Solutions of caustic soda and potash up to 38° Tw exert approximately the same shrinking action on cotton, but from 38°–55° Tw. caustic soda produces a greater shrinkage.

Lithium hydroxide had a greater mercerising action, as measured by shrinkage, than caustic soda and potash in solutions of low concentrations. Ammonia up to 0·880 sp. gr had no swelling or contracting action at all Saturated solutions of calcium, strontium and barium hydroxides were also ineffective.

More recently, the behaviour of cotton towards caustic potash has been investigated by Collins and Williams (*Journ. Text. Inst*, 1924, xv. 149). As in a previous investigation of this kind with caustic soda (see page 56) individual cotton hairs

FIG. 23.—CHANGE IN LENGTH OF COTTON YARN WHEN IMMERSED IN SOLUTIONS OF CAUSTIC SODA AND POTASH.
(Knecht and Harrison)

were examined and similar methods were employed

—•——•— *Water and Soda-boiled Cotton Hairs.*
---o---•--- *Raw Cotton Hairs.*
·•· · o···· *Yarn (Knecht and Harrison).*
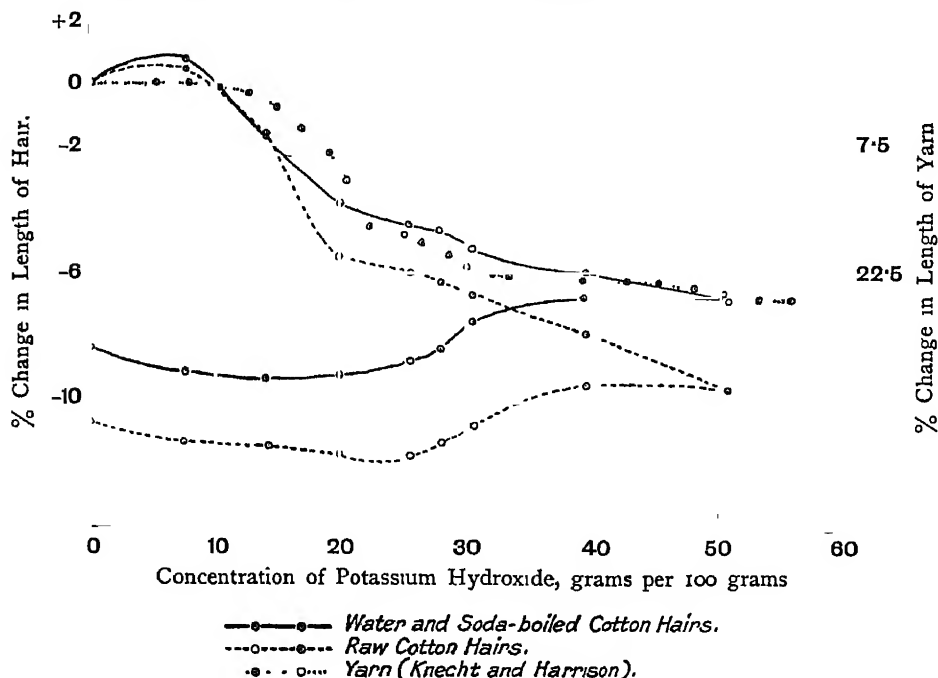
FIG. 24.—CHANGE IN LENGTH OF COTTON HAIRS IN CAUSTIC POTASH.
(Collins and Williams.)
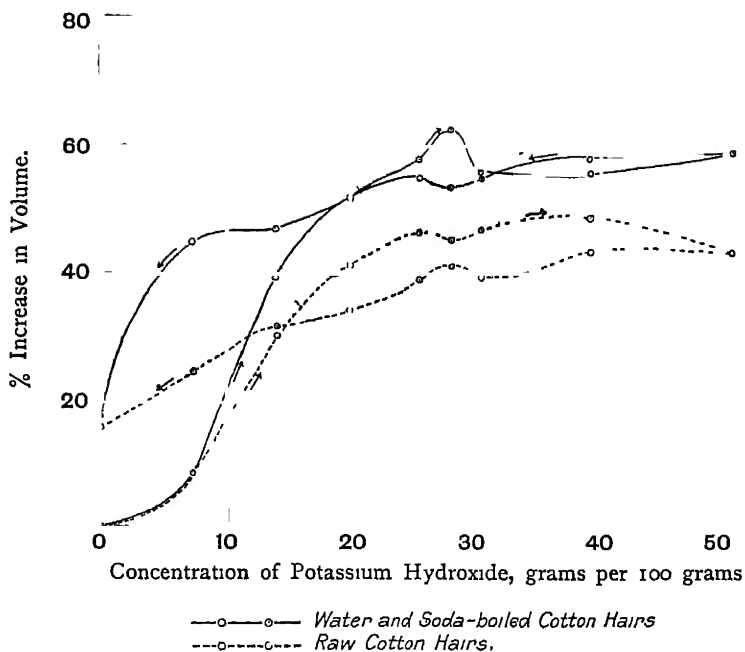
FIG 25.—CHANGE IN VOLUME OF COTTON HAIRS IN CAUSTIC POTASH.
(Collins and Williams)
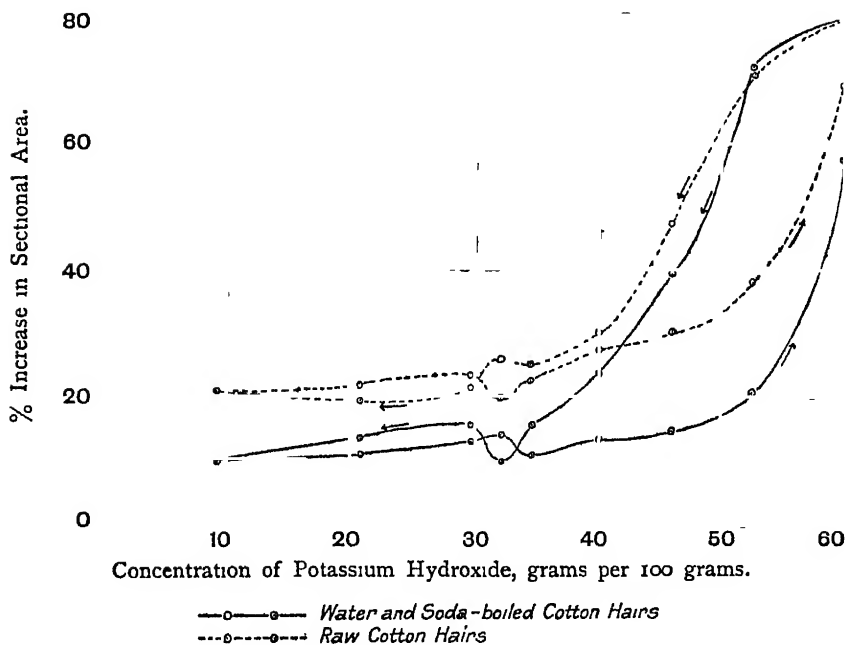
FIG. 26 —CHANGE IN SECTIONAL AREA OF COTTON HAIRS IN CAUSTIC POTASH.
(Collins and Williams)

The results shown below and in Figs 24, 25 and 26 were obtained by immersing cotton hairs in water, then in solutions of caustic potash of increasing
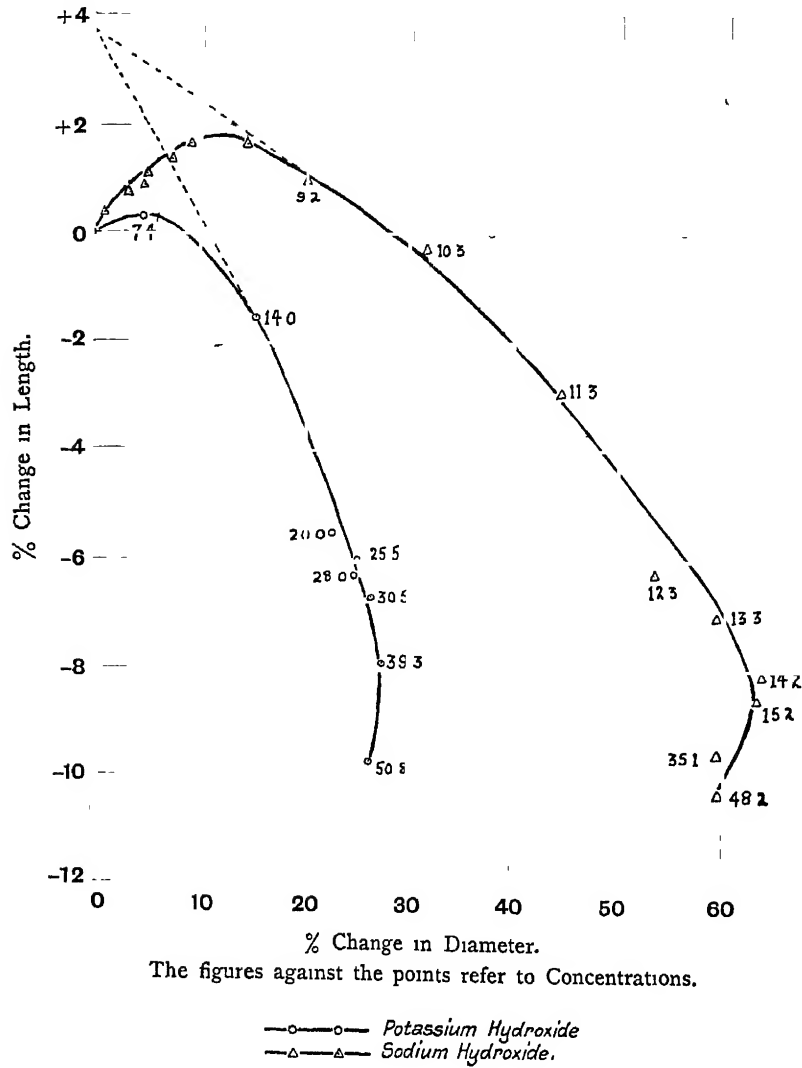
FIG 27.—RATIO BETWEEN MEAN DIAMETER AND LENGTH OF COTTON HAIRS
IN CAUSTIC SODA AND POTASH.

(Collins and Williams)

concentration, then in solutions of decreasing concentration and finally in water. The same Trinidad cotton was used throughout the experiments, but one part of it was previously subjected to a water- and soda-boil.

It is evident that cotton hairs suffer an extension in length when immersed in solutions of caustic potash of low concentration, thus resembling their behaviour in similar solutions of caustic soda. The non-reversible nature of the process of mercerisation is also evident

—o——o— % Change in Diameter, KOH
---o---o--- % " " Length, KOH.
—△——△— % " " Diameter, NaOH.
---△----△--- % " " Length, NaOH
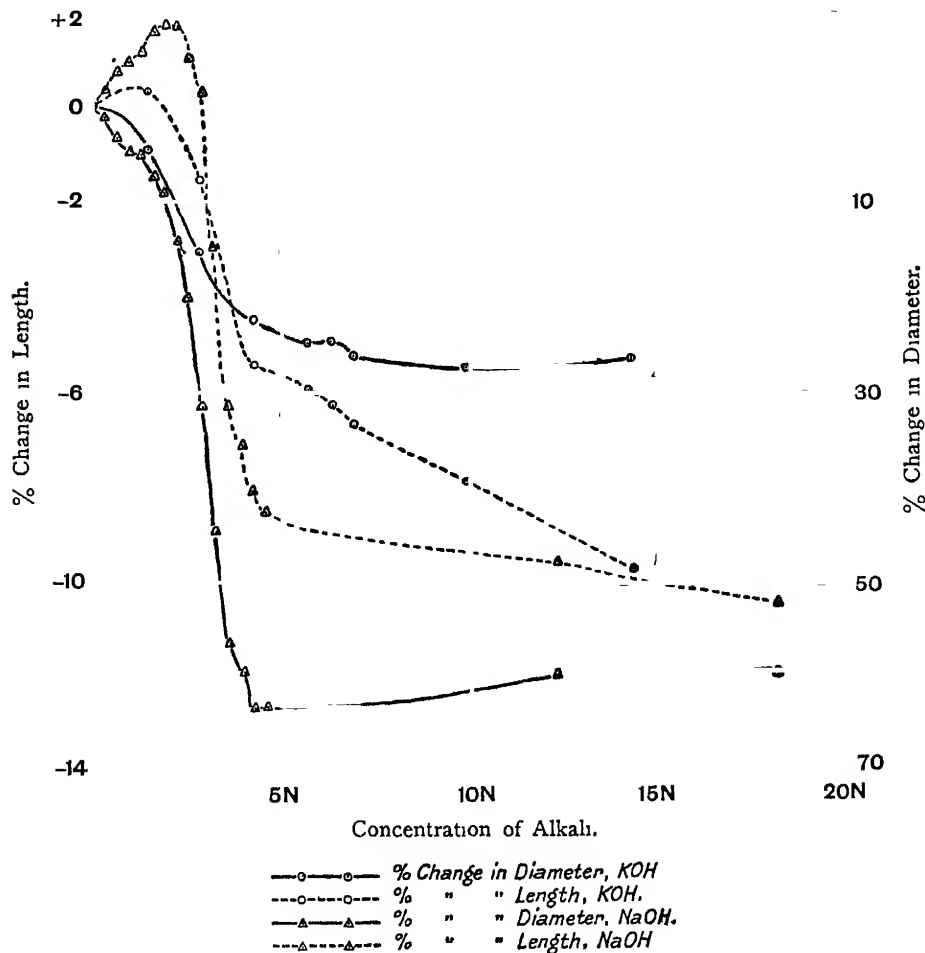
FIG. 28 —CHANGES IN LENGTH AND DIAMETER OF COTTON HAIRS IN CAUSTIC SODA AND POTASH

(Collins and Williams)

From Fig 27 it will be gathered that the average increase in diameter which cotton hairs suffer when immersed in caustic potash is less than half that which occurs in caustic soda, although the increase in length is of the same order. Cloth mercerised with caustic potash should therefore have a less full handle than that mercerised with caustic soda.

TABLE XXII

MERCERISATION OF RAW COTTON HAIRS

Increasing Concentrations.

Per cent KOH	0·0	7·4	14·0	20·0	25·5	28·0	30·5	39·3	50·8
Per cent change in length	0·0	+0·27	−1·53	−5·42	−5·96	−6 25	−6·66	−7·87	−9 66
Per cent. change in cross-section	0·0	9·1	32·8	50·1	56·1	55·7	59·2	62·2	59·6
Per cent. change in volume	0·0	8·8	30·3	41·3	46 4	45·4	47·9	49·0	43·6

Decreasing Concentrations

Per cent KOH	39·3	30·5	28·0	25·5	20·0	14·0	7·4	0
Per cent change in length	−9·47	−10·75	−11·26	−11·67	−11·63	−11·54	−11·31	−10 67
Per cent change in cross-section	58·7	57·0	60·2	58·0	53·0	50·0	42·3	10·9
Per cent change in volume	43·4	39·5	41 1	39·1	34·5	32·0	24·9	1·6

TABLE XXIII

MERCERISATION OF SCOURED COTTON HAIRS

Increasing Concentrations

Per cent KOH	0·0	7·4	14·0	20·0	25·5	28·0	30·5	39·3	50·8
Per cent. change in length	0·0	+0·60	−1·62	−3·78	−4·44	−4 64	−5·20	−5·97	−6·95
Per cent change in cross-section	0·0	8·0	41·0	57·0	65·2	70·8	65·0	67·1	70·7
Per cent. change in volume	0·0	8·5	39·8	52·1	58·1	62·8	56 2	56·1	59·2

Decreasing Concentrations.

Per cent KOH	39·3	30·5	28·0	25·5	20·0	14·0	7·4	0
Per cent. change in length	−6·74	−7·49	−8·31	−8·75	−9·15	−9·28	−9·09	−8·32
Per cent change in cross-section	69·6	67·8	66·7	69·8	67·1	66·1	60·0	22·4
Per cent. change in volume	58 2	55·4	53·5	55·2	52·0	47·3	45·3	17·6

Maximum swelling occurs in 28 per cent. caustic potash and in 15 per cent. caustic soda ; this agrees with Ristenpart's results, and it is also significant that this maximum swelling occurs in solutions having the maximum specific electrical conductivity.

In the course of more extended investigations, Nodder and Kinkead (*Journ.*
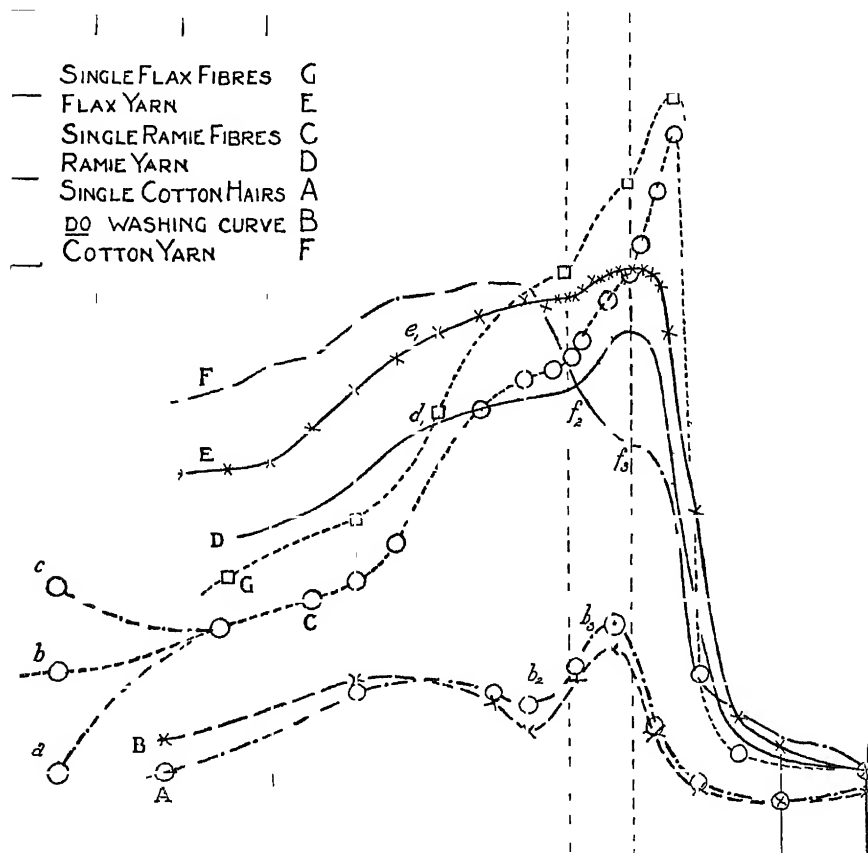
Fig 29 —Changes in Length of Cotton, Flax and Ramie in Caustic Soda.

(Nodder and Kinkead)

Text Inst, 1923, xiv. 142) have compared the behaviour of cotton hairs and yarn with that of flax and ramie hairs and yarns   The results are expressed in Fig 29.

The changes of volume, length and diameter of cotton hairs during mercerisation such as have been described above, are, of course, accompanied by considerable changes in shape and appearance   Essentially, the change of shape is that of a flat, twisted ribbon to an oval or cylindrical rod, the oval form being obtained by mercerisation without tension and the circular form with tension.   At the

same time, the characteristic lumen of the natural hair frequently disappears or becomes very much contracted.

Pope and Huebner (*Journ. Soc Chem. Ind* , 1904, xxiii. 404) give a detailed description of their observations of cotton hairs during mercerisation under different conditions. These observations are summarised thus

<center>TABLE XXIV</center>

Strength of NaOH	Behaviour of Cotton Hair
0°–15° Tw . .	No change
16°–18° . .	Hair incompletely untwists during about one second
20° . .	Initial rapid untwisting which then continues very slowly.
26° . .	Rapid untwisting, lasting for 5 seconds
35° . .	Untwisting followed by swelling
40° . .	Untwisting and swelling occur together
60°–80° . .	Swelling precedes untwisting and nearly all the hairs are seen to burst or split

When treated with cuprammonium solution, mercerised cotton hairs swell uniformly (see page 29).

Cotton Strength and Alkalis.

Mercerisation also affects the strength of cotton hairs and yarns—generally the strength is increased   The results of Ristenpart (see page 61) indicate that yarn mercerised without tension by means of caustic soda or potash has an increased breaking strain of nearly 40 per cent.   Pope and Huebner (*Journ Soc Chem Ind* , 1903, xxii 70) found an increase of 26 per cent for yarn mercerised in 31 per cent caustic soda for 24 hours.   Marshall (*Journ. Soc Dyers & Col.,* 1924, xl. 11) gives the following results obtained by mercerisation without tension :

<center>TABLE XXV</center>

Strength of NaOH	Breaking Strain of Cotton Hank
0° Tw . . .	26 33 lb.
10°	25·66
20°	24 00
30°	29 50
40°	27·33
50°	21 00
60°	22·75
70° . . .	21 00
80°	20·66

These indicate that there is a gain or loss of strength according to the strength of the mercerising liquor.

Most workers agree that there is a general increase of strength when mercerisation of yarn is effected with tension. Greenwood (*Journ Text Inst*, 1919, x. 274) indicates some results he obtained with Egyptian cotton yarn

TABLE XXVI

Yarn.	Breaking Strain
Grey, unmercerised	10 87 ounces
„ mercerised under tension. . .	12·86 „
„ „ without tension . .	12·48 „
Bleached, unmercerised	11·62 „
Mercerised under tension and bleached .	12 83 „

Corser and Turner (*Journ. Text. Inst*, 1923, xiv. 332) find that the gain in strength of twofold yarns on mercerisation increases up to a point with increase in the mercerising tension, and that the strength of twofold yarns, made from single yarns having a given twist, increases up to a point with the doubling twist for grey yarns, but decreases with the doubling twist for mercerised yarns. They quote the following results

TABLE XXVII

Observer.	Yarn.	Mercerisation.	Increase in Strength.
Buntrock . .	2/40's.	Without tension.	68 per cent
„ . .	„	With tension	35 „
Huebner and Pope	2/50's Egyptian	Without tension	40 „
„ „	2/38's Sea Island	With tension (static)	12·4 „
Bowman . .	2/60's Egyptian	With tension	49 „
„ . .	2/80's „	Without tension	23 „
„ . .	„ „	With tension.	{ 20% (Baer) { 6% (Moscrop)
Lowe . . .	2/60's	With tension	10–40 per cent

Corser and Turner add, however, that the theory that the strength phenomena of mercerised yarns are due to increased frictional resistance between the fibres affords a satisfactory explanation of the differences in behaviour between grey and mercerised yarns and also of the differences in behaviour between the fabrics made from these yarns respectively. Results obtained with yarns cannot therefore be indiscriminately applied to the individual cotton hairs.

Greenwood gives the following results obtained on hairs taken from mercerised and grey yarns

TABLE XXVIII

Single Hairs from	Breaking Strain.	
	First Series	Second Series.
Grey yarn	6·77 g	6·83 g.
„ mercerised without tension .	6·87	6·35
„ „ under tension	6 60	6·30
Bleached yarn	5·32	5·82
„ mercerised . . .	5 79	5·40

These results are not very conclusive Clibbens (*Journ. Text Inst*, 1923, xiv. 231) quotes a private communication from Willows, giving the following results (the mean of about 30 determinations) for the breaking loads and extensibilities of hairs from scoured Egyptian sliver before and after mercerisation without tension in 20 per cent. caustic soda ·

TABLE XXIX

	Breaking Strain	Extension at Break.
Original scoured Egyptian cotton . .	7 2 g.	7·4 per cent.
„ mercerised without tension	6·7	12·2 „

Finally, Clegg (*Journ. Text Inst*, 1924, xv 6) has sought to clear up these conflicting results Cotton hairs were mercerised in caustic soda of 40° Tw.

without tension, washed and dried and the breaking load determined on a suitable number. Her results show an increase in the mean breaking load of single hairs of 11·8–49·2 per cent and, simultaneously, the hairs become more uniform in strength. Another point is that there is a decrease in the number of very weak hairs after mercerisation.

On the whole, it may be concluded that cotton yarns and hairs have an increased strength after mercerisation with and without tension

Cotton Lustre and Alkalis.

From a technical standpoint, however, the most important feature of mercerisation is that it produces increased lustre Mercerisation is much more frequently carried out for this purpose than for the increase of dyeing capacity which mercerised cotton possesses

Many workers have endeavoured to correlate the behaviour of cotton hairs during mercerisation with their resulting lustre, but, in spite of much evidence relating to the disappearance of twist, it seems that the increased lustre is almost entirely due to the smooth rodlike form of the mercerised hair This is supported by the fact that no increased lustre is obtained unless mercerisation is carried out under tension , and, as stated previously, mercerisation under tension is more favourable to the production of hairs having circular cross-section than is mercerisation without tension

Shrinkage during mercerisation is a difficulty in technical practice, and necessitates the use of special machinery such as that shown in Fig 30 (for fabrics) and in Fig 31 (for yarns) ; but it is generally admitted that mercerisation without shrinkage, such as may be produced by adding such substances as ether, sodium silicate, glycerine and sodium sulphide to the caustic alkali, does not lead to the production of maximum lustre

The temperature of mercerisation has a considerable effect on lustre, although contradictory results have been obtained Thus, Huebner and Pope (*Journ Soc Chem Ind*, 1904, xxiii. 404) state that the lustre produced on Egyptian yarn when mercerised with caustic soda of 50° Tw is much less marked than that produced at ordinary temperature. Beltzer (*Rev Gen Mat Col*, 1902, vi 25) maintains that the same lustre is obtained by mercerisation with 66° Tw caustic soda at 15° C and 90° C , although a more transparent yarn is produced at the higher temperature Harrison (*Journ Soc Dyers & Col*, 1919, xxxi 198) reports that the lustre of cotton mercerised with caustic soda of 50° Tw. at 90° C is slightly less than that of cotton similarly mercerised at 20° C.

Knecht and Harrison (*Journ Soc Dyers & Col*, 1912, xxviii 224) compared the lustre of cotton yarns mercerised by means of caustic soda and potash at different temperatures, the yarns being treated while wound on an iron frame so as to prevent shrinkage They found that caustic soda of 95° Tw and caustic potash of 123° Tw , both produced a better lustre at 80° C than at 16° C , in each

6

instance, potash produced the better lustre, but its superiority was less at the higher temperature   They also found that caustic soda of 55° Tw and caustic potash of 66° Tw had the same lustring effect at ordinary temperatures, but the former alkali produced a better lustre at 10° C than at 80° C

It is by no means certain that the increase of lustre is proportional to the degree of shrinkage, but it is found that caustic soda exerts a greater shrinkage at lower temperatures

Until recently, practically all observations concerning the lustre of textile materials have been based on the investigator's judgment—a doubtful factor. Oxley has now designed apparatus (*Journ. Soc Dyers & Col*, 1924, xl 135) for the quantitative measurement of lustre of yarns and fabrics, so that in the future more definite results concerning lustre and mercerisation may be possible

Cotton Dyeing and Power Alkalis.

It will be remembered that Mercer's interest in mercerisation was largely concerned with the increased dyeing power which he found the mercerised cotton to possess   Mercerised cotton is found to have a definitely greater affinity for direct cotton dyes (not basic dyes) than unmercerised cotton, and this subject has been investigated by Knecht (*Journ Soc Dyers & Col*, 1908, xxiv 67 and 107), who has also discovered the most convenient method for estimating direct dyes by means of titanous chloride (*New Reduction Methods of Analysis,* Knecht and Hibbert).

In these experiments, Knecht mercerised Egyptian yarn under different conditions, it being afterwards washed and dried.   The yarn was then dyed with 3 per cent of Benzopurpurin 4B and the dyestuff absorbed determined.   The following results were obtained

TABLE XXX

Concentration of NaOH used in Mercerising Liquor		Absorption of Benzopurpurine 4B per 100 g of Cotton
0 0 per cent or	0° Tw	1 77 g
4·5	,, 10°·4	1 88
8·5	,, 19° 0	2·49
11 0	,, 25° 0	2 57
13·5	,, 30°·4	2·95
15·5	,, 35°·1	3·02
17·5	,, 37°·5	3·15
20 0	,, 45° 0	3 27
22·5	,, 50° 4	3 38
25·0	,, 55° 0	3·50
27 0	,, 60° 0	3·56
29·0	,, 64°·2	3 60
31 5	,, 69°·4	3 66
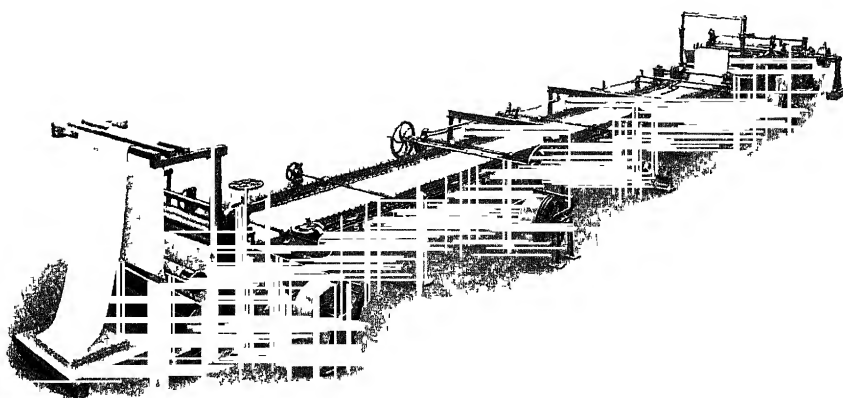
FIG 30.—MACHINE FOR MERCERISING COTTON FABRICS
(Sir J Farmer, Norton & Co. Ltd)
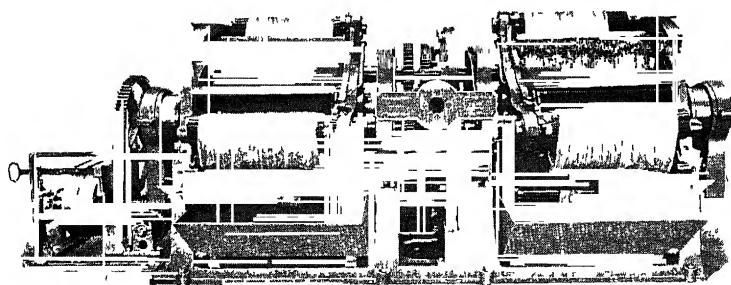
FIG 31 —CENTONIP MERCERISING MACHINE
(S Spencer & Sons Ltd)
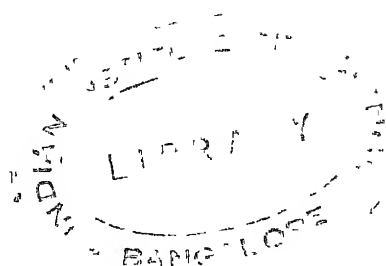
The dyeing capacity thus increases with increase in the strength of the mercerising liquor   A similar result (not so accurately determined, however)
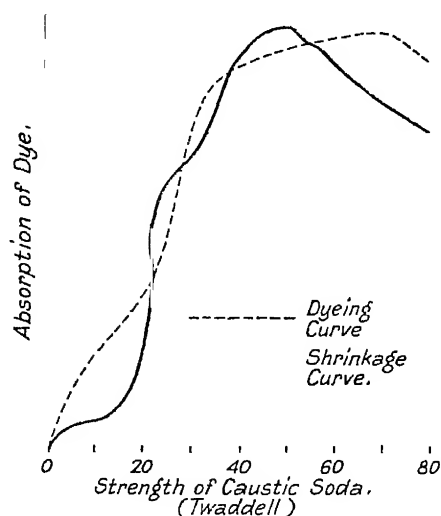
FIG 32 —CURVE SHOWING INCREASE OF DYEING CAPACITY OF COTTON
PRODUCED BY MERCERISATION.

(Huebner and Pope.)

was obtained by Huebner and Pope (*Journ Soc. Chem Ind*, 1904, xxiii 404) and is shown in Fig 32.

Interesting results were also obtained in an investigation of the time necessary for completion of the mercerisation process, the progress of this being followed by determination of the dyeing capacity of the cotton under treatment, thus

TABLE XXXI

Duration of Mercerising Process	Shrinkage	Absorption of Benzopurpurine 4B
5 seconds	15 7 per cent	3 24 per cent
10 ,,	17 4 ,,	3 62 ,,
20 ,,	25 0 ,,	3 80 ,,
40 ,,	25 0 ,,	3 89 ,,
60 ,,	25 0 ,,	3 91 ,,
180 ,,	27 0 ,,	4 10 ,,

Mercerisation being effected with 50° Tw caustic soda.

The tension on cotton during mercerisation also affects its dyeing capacity thus

TABLE XXXII

	Benzopurpurine 4B Absorbed	
	Unbleached	Bleached
Unmercerised cotton . .	1 55 per cent	1 50 per cent
Mercerised with tension . . .	2 90 ,,	2 86 ,,
,, without tension . .	3·39 ,,	3 54 ,,

Again, the drying of mercerised cotton generally reduces its dyeing capacity thus

Egyptian yarn was mercerised without tension in 37° Tw caustic soda and then washed and dyed

TABLE XXXIII

Yarn.	Per cent Benzopurpurine Absorbed	Per cent Chrysophenine Absorbed
Mercerised, dyed without drying . . .	3 24 per cent	0 96 per cent
,, air dried before dyeing .	3·03 ,,	0·92 ,,
,, dried at 110° C. before dyeing .	2 51 ,,	0·84 ,,
Unmercerised yarn	1 77 ,,	0 58 ,,

In another experiment, two skeins of American bleached cotton yarn were mercerised in 45° Tw. caustic soda, washed, acidified and washed till neutral One skein was dyed directly, the other after drying for one hour at 100°–110° C The dyeing capacities of these two skeins were then found to be

TABLE XXXIV

	Benzopurpurine 4B Absorbed
Yarn mercerised, dried at 110° C . .	1 16 per cent
,, ,, not dried	1 74 ,,

It was then shown that unmercerised cotton was not affected by these treatments thus ·

TABLE XXXV

Yarn	Benzopurpurine 4B Absorbed
Steeped in water for 24 hours and dyed without drying	1·76 per cent.
,, ,, ,, air dried before dyeing	1·79 ,,
,, ,, ,, dried at 110° C before dyeing	1 80 ,,

Finally, some bleached American yarn was mercerised without tension in 50° Tw caustic soda, treated as below and dyed :

TABLE XXXVI

Yarn	Absorption of Benzopurpurine 4B	Absorption of Chrysophenine.
Mercerised, dyed without drying . .	2·49 per cent	0·97 per cent
,, air dried before dyeing	1·57 ,,	0 77 ,,
,, dried at 100° C. before dyeing	1·27 ,,	0·54 ,,
Unmercerised yarn . .	0·80 ,,	0·31 ,,

It is therefore quite evident that drying decreases the dyeing capacity of cotton for dyestuffs, and the decrease is greater as the temperature of drying is increased.

Knecht also compared, by dyeing tests, the action of caustic soda and potash on cotton Skeins were mercerised under similar conditions with 50° Tw. solutions of these alkalis and subsequently dyed with direct dyes such as Diamine Green, Chrysophenine and Benzopurpurine 4B He found that the shades on cotton skeins mercerised with caustic soda were four times, and on skeins mercerised with caustic potash twice as deep as those on untreated skeins

Although all strengths of alkali have some effect on cotton, Pope and Huebner (*Journ. Soc Chem Ind*, 1904, xxiii 404) found that kier-boiling of cotton yarn with 2° Tw caustic soda did not appreciably affect its affinity for direct cotton dyestuffs

One feature of mercerisation on a large scale which is soon noticed, is that the immersion of cotton, and particularly grey cotton (containing starch impurities), in caustic soda liberates considerable quantities of heat. This phenomenon has been very carefully investigated by Barratt and Lewis (*Journ Text.*
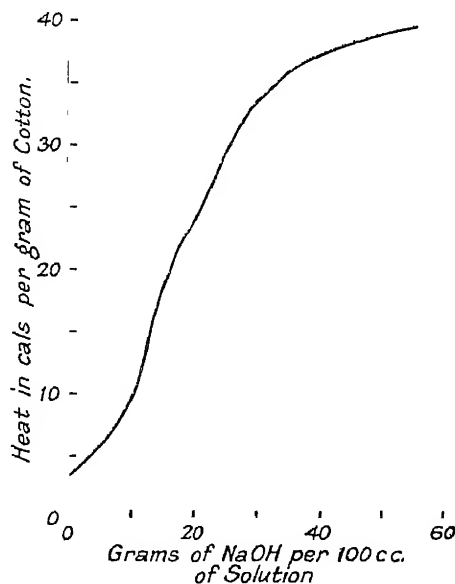
FIG. 33 —CURVE SHOWING HEAT LIBERATED BY COTTON DURING MERCERISATION

[(Barratt and Lewis)]

Inst, 1922, xiii 17) using electrical methods for measurement of the heat. Their results, showing the heat liberated when scoured cotton sliver is immersed in solutions of caustic soda of various concentrations, are given below and shown in Fig. 33.

TABLE XXXVII

Strength of Alkali	Heat Liberated			Strength of Alkali	Heat Liberated
0° Tw	3·6 cals. per g of cotton			46° Tw.	29·5 cals
16°	6·7	,,	,,	,,	48°	31·4 ,,
21°	9·3	,,	,,	,,	61°	33·8 ,,
26°	16·1	,,	,,	,,	63°	36 7 ,,
36°	22·5	,,	,,	,,	84°·5	39·0 ,,
40°	25·9	,,	,,	,,	..	..

Two definite inflexions in the curve indicate that there is a marked liberation of heat when the concentration of the mercerising alkali reaches 10 per cent. (22° Tw) and 15 per cent. (34° Tw)

Cotton Moisture Content and Alkalis.

Ordinary cotton normally contains about 7 per cent of moisture, although this, of course, varies with the humidity of the surrounding atmosphere   It is found that mercerised cotton generally has a moisture content of 11 per cent. Miller (*Ber* , 1911, xliv 728) records the following values

Unmercerised cotton	.	.	.	7·12 g water/100 g cotton
Mercerised cotton .	.	.		10·0 g water

It is evident, however, that the moisture content is dependent on the conditions of mercerisation, for Schwalbe (*Zeit angew Chem* , 1909, xxii 197) gives the following

<div align="center">

TABLE XXXVIII

</div>

Concentration of Mercerising Liquor	Moisture Content of Cotton (calc on Dry Cotton)
o per cent NaOH	6 1 per cent
8 ,, ,,	7 7 ,,
16 ,, ,,	10 7 ,,
24 ,, ,,	11 3 ,,
40 ,, ,,	12 1 ,,

Coward and Spencer (*Journ Text Inst* , 1923, xiv 41) have investigated the moisture content of mercerised cotton from another interesting standpoint by use of a centrifuge (see page 84).   They find that when loose cotton is mercerised, washed in water, neutralised with very dilute acid and again thoroughly washed in water, its absorption of water (measured by steeping it in water and then removing interfibrillar water by centrifuging) is greater than similar but unmercerised cotton

The absorption of water is found to be dependent on the conditions of mercerisation and also on the treatment of the cotton after mercerisation , the moisture content is also related to the dyeing capacity (see page 74)   The results also closely agree with some values for the hygroscopic moisture determined by Higgins (*Journ Soc Chem Ind* , 1909, xxviii 188) by treating cotton yarn with various strengths of caustic soda, washing, drying and exposing it for a considerable time to the air   Coward and Spencer's results are shown in Fig 34 and compared with those of Knecht and Higgins in Fig 35

Mercerisation increases the water absorptive properties of cotton, but this effect is largely reduced when the mercerised cotton is dried. All evidence thus shows the important effects produced by drying cotton after mercerisation.
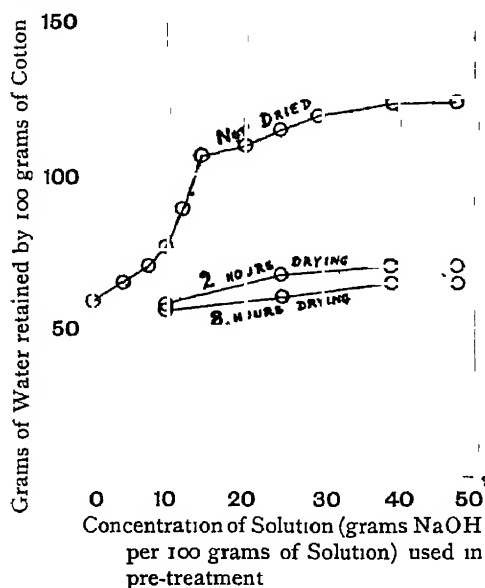
FIG. 34.—WATER ABSORPTION OF COTTON HAIRS AFTER MERCERISATION
(Coward and Spencer.)
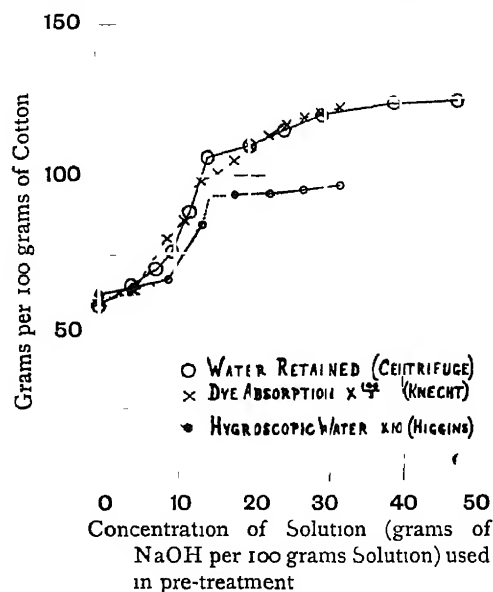
FIG. 35 —COMPARISON OF WATER ABSORPTION, DYE ABSORPTION AND HYGROSCOPICITY OF COTTON AFTER MERCERISATION
(Coward and Spencer Knecht Higgins)

Huebner has also discovered (*Journ Soc Chem Ind*, 1908, xxvii 105) that the increased moisture content of mercerised cotton is closely related to its increased absorption of iodine from solutions containing iodine and potassium iodide. Using an N/100 solution of iodine and immersing cotton in it for 48 hours, he found the absorption to take place as indicated in the following table, which also includes the moisture contents

TABLE XXXIX

Cotton		Absorption calculated on Weight of Cotton	
		Iodine	*Water*
Bleached, untreated . . .		0 29 per cent	5 88 per cent.
,, mercerised with tension	.	0 36 ,,	7·45 ,,
,, ,, without tension	.	0·42 ,,	8·36 ,,
Unbleached, untreated . .		0 30 ,,	6 12 ,,
,, mercerised with tension		0·42 ,,	7·65 ,,
,, ,, without tension	.	0·46 ,,	8·53 ,,

As yet, no adequate explanation of the increased absorptive power of mercerised cotton has been put forward ; more investigation is required

Cotton and Alkalis : Absorption or Chemical Combination ?

Although the main features of mercerisation have been applied to industry on a very large scale, it is surprising that the chemistry of the process, though investigated for over seventy years, is still undetermined   It has yet to be
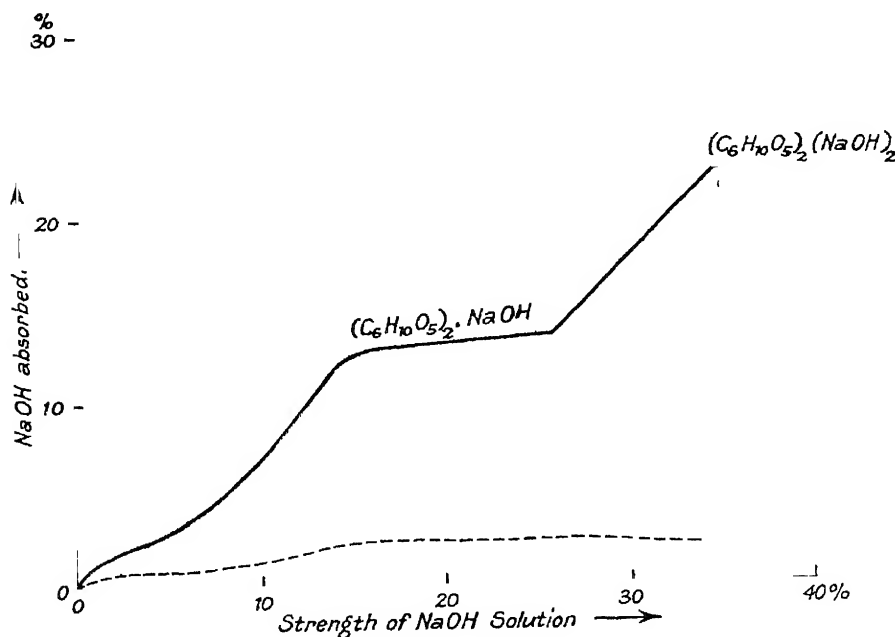
FIG. 36 —ABSORPTION OF CAUSTIC SODA BY COTTON
(Vieweg)

decided whether or not cellulose forms definite chemical compounds with caustic alkalis.

Mercer considered that cellulose combined chemically with caustic soda, the resulting compound being so unstable that it could be completely destroyed by washing in water   Subsequently Gladstone (*Journ Chem Soc*, 1852, v 17) took an interest in the process   He considered that uncombined caustic soda could be removed from the mercerised cotton by washing it with alcohol , the composition of the remaining cellulose compound could then be determined by conversion of the alkali into sodium sulphate   In this manner Gladstone obtained evidence of the formation of the compounds—$(C_6H_{10}O_5)_2$ NaOH and $(C_6H_{10}O_5)_2$ KOH He obtained the former compound by treatment of cotton with caustic soda of

sp. gr 1·342 and the latter by use of the strongest solution of caustic potash which remained limpid

Several years later, Vieweg (*Ber*, 1907, xl 3877) again investigated the process of mercerisation His method consisted of placing 3 g of cotton, dried at 90° C, in a flask containing 150 c c of a solution of caustic soda, at room temperature, shaking for 1 hour and standing 2 hours The alkali content of the supernatant liquor was determined before and after the addition of the cotton
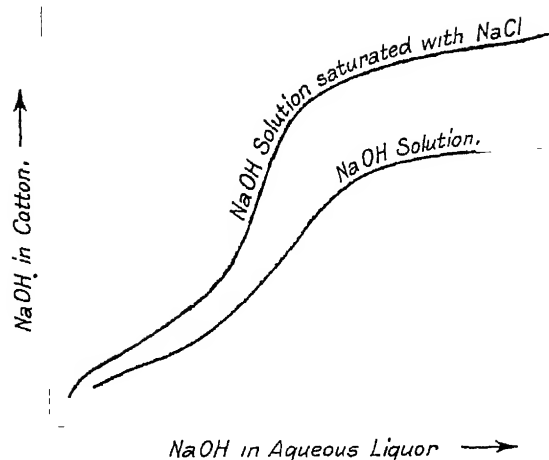
FIG. 37 —ABSORPTION OF CAUSTIC SODA BY COTTON IN
THE PRESENCE OF SALT.
(Vieweg)

In this manner Vieweg was able to calculate the alkali absorbed by the cotton, and his results are shown in Fig. 36.

Two definite inflexions occur in the curve corresponding to the compounds $(C_6H_{10}O_5)_2$ NaOH and $(C_6H_{10}O_5)_2.2$NaOH and Vieweg believed that these were definitely formed during mercerisation. Also, he showed that such alkali cellulose compounds were capable of reacting with benzoyl chloride to form cellulose benzoates.

Vieweg also determined the alkali absorbed by previously mercerised and washed cotton, when immersed in 2 per cent. caustic soda, and found it to vary with the conditions of the pre-mercerisation Cotton mercerised with strong caustic soda solutions was found to be capable of absorbing more caustic soda (from the 2 per cent solution) than cotton mercerised

FIG 38.—ABSORPTION OF CAUSTIC SODA BY
COTTON HAIRS
(Joyner)

with weak solutions These results are shown by the lower curve in Fig. 36, and such a curve may be used as the basis of a method for determining the conditions of mercerisation of any sample of mercerised cotton.

Subsequently, Vieweg (*Ber* , 1908, xlii 3269) discovered that the addition of salt to the mercerising liquor considerably increased the amount of alkali absorbed by the cotton ; but this discovery found no application in technical mercerisation, because an inferior lustre was obtained. The effect of the addition of salt is shown in the curves in Fig 37

About the same time, Miller (*Ber* , 1907, xl. 4902, and 1908, xli. 4297) also investigated the process of mercerisation, and, as a result, concluded that except in very dilute and very strong solutions of caustic soda, the alkali suffers a constant partition between the cellulose and the water of solution. He thus opposed the existence of chemical compounds between cellulose and a caustic alkali.

Miller's conclusions have been largely accepted by Huebner and Teltscher (*Journ. Soc Chem Ind* , 1909, xxviii 641) and by Joyner (*Journ Chem Soc Trans* , 1922, cxxi. 2395) The latter investigator carried out his experiments in much the same manner as did Vieweg, immersing cellulose (about 1 g) in caustic soda (about 10 c.c) at room temperature and determining the absorption of alkali by titration of the alkaline solution before and after. His results are given below and also expressed in Fig 38

TABLE XL

Composition of Aqueous Phase	Composition of Cellulose Phase.
Grams of NaOH per 100 g of water	Grams of NaOH per 100 g of cellulose
29·6	16 6, 17·8
28 6	14 1, 16 5
24·3	15·7
20·5	13 9
19·1	12·8
18·8	12·6, 12 8
13·3	9 9
12·8	8·6
7·65	3·41
6·95	3·23
4·02	1 72
3·79	2 20, 2 27, 2·15

The shape of the curve suggests that no definite alkali-cellulose compounds are formed Joyner also confirmed the observation of Vieweg that addition of

salt and other neutral salts to the mercerising liquor increased the absorption of alkali by the cellulose   Thus

TABLE XLI

Composition of Solution				Absorption of NaOH by Cellulose (100 g)
NaOH	NaCl	NaNO$_3$	Water	
7 1	..	.	92·9	3 41 g
6 5	6·8		86 7	5 11
6 0	13 6		80 4	5·40
5·3	22·4		72·3	5 95
4·2	13 7	23 1	59·0	6 40

Leighton (*Journ. Phys Chem.*, 1916, xx. 32) investigated the process of mercerisation, using a centrifuge to separate the liquid phase from the cellulose phase   His results are not free from criticism, so that those obtained by a similar method by Coward and Spencer (*Journ. Text Inst*, 1923, xiv. 32), but probably more accurate, will be considered here

These investigators first showed that by means of a centrifuge 8·2 cm in diameter and running at 7000–8000 r p m , liquids having the viscosity of ordinary mercerising liquors could be practically completely removed from the surface of loose cotton.   They were therefore able to immerse cotton in various solutions of caustic soda, remove all external liquor by centrifuging, and then determine by weighing and titration the amounts of water and sodium hydroxide in the mercerised cotton   Their results for scoured Egyptian sliver are given here :

TABLE XLII

Strength of Mercerising Liquor.				Absorption (100 g. Cotton).		
				Total	Water	NaOH.
0·0 g NaOH per 100 g of solution				52·3 g	52·3 g	0·0 g.
4·0 ,,	,,	,,	,,	73 5	67 9	5 6
7 4 ,,	,,	,,	,,	99 8	88 7	11·1
9·4 ,,	,,	,,	,,	133 3	116 0	17 3
11·9 ,,	,,	,,	,,	177	150 8	26 2
14 3 ,,	,,	,,	,,	222	180 4	41·6
20·1 ,,	,,	,,	,,	220	166·8	53·2
24 4 ,,	,,	,,	,,	239	169 5	69 5
29 3 ,,	,,	,,	,,	236	153·1	82 9
39 0 ,,	,,	,,	,,	251	138·1	112·9
48 8 ,,	,,	,,	,,	288	133·0	155·0

The absorption of alkali by fabric was determined in a similar manner, the following results being obtained

TABLE XLIII

Strength of Mercerising Liquor				Absorption (100 g of Cotton).		
				Total	Water	NaOH
0 0 g NaOH per 100 g of solution				52 7 g	52 7 g	0·0 g
4 0	,,	,,	,,	70 6	65 8	4 8
7·4	,,	,,	,,	86 4	77 0	9·4
9 4	,,	,,	,,	94 0	81·1	12·9
11·9	,,	,,	,,	106 5	87·5	19 0
14·3	,,	,,	,,	114 3	88·5	25·8
20·1	,,	,	,,	121·2	86·4	34·8
24 4	,,	,,	,,	126·5	83 8	42 7
29·3	,,	,,	,,	136·2	83 4	52 8
39 0	,,	,	,,	143·6	72 8	70·8
48·8	,,	,,	,,	158·2	64 1	94·1

These results and the corresponding curves shown in Figs 39 and 40, indicate that cotton in the form of yarn and fabric is unable to swell and absorb as much alkaline liquor as loose cotton under similar conditions   It is also evident that
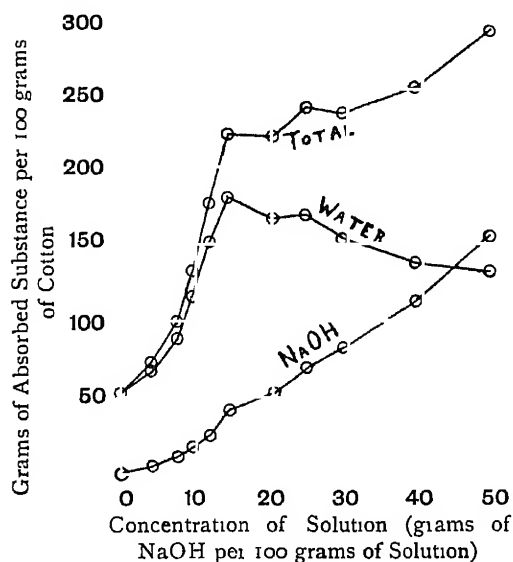
FIG. 39.—ABSORPTION OF CAUSTIC SODA BY
COTTON HAIRS
(Coward and Spencer)
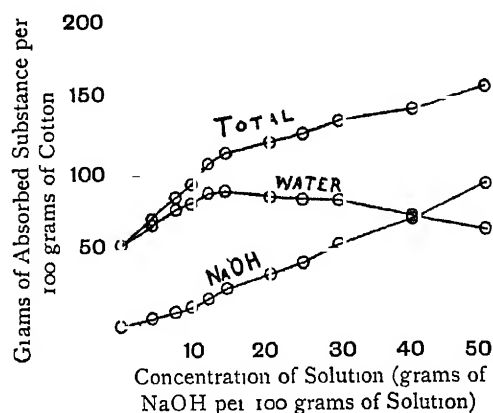
FIG 40 —ABSORPTION OF CAUSTIC
SODA BY COTTON FABRIC
(Coward and Spencer)

14 per cent is a critical strength of caustic soda, for it separates each curve into two distinct portions.

By calculation from the above figures, the amounts of caustic soda preferentially absorbed by loose cotton and cotton fabric were obtained thus

TABLE XLIV

Strength of Mercerising Liquor.	Preferential Absorption of NaOH (100 g Cotton)	
	Loose Cotton	Fabric
0·0 g NaOH per 100 g of solution	– g	– g
4 0 ,, ,, ,,	2·9	2·1
7 4 ,, ,, ,,	4·3	3 4
9 4 ,, ,, ,,	5·9	4 7
11 9 ,, ,, ,,	6·7	7 5
14 3 ,, ,, ,,	13·6	11·6
20 1 ,, ,, ,,	12·9	13·5
24 4 ,, ,, ,,	17·3	16 4
29 3 ,, ,, ,,	22·6	19 2
39 0 ,, ,, ,, .	28·6	25 5
48·8 ,, ,, ,,	33 0	34 8

The corresponding curves are shown in Fig 41

These investigations of Coward and Spencer, probably more accurate and certainly more informative than others previously carried out, still leave the chemistry of the process of mercerisation undecided For, though these workers conclude that the results yield no definite evidence of the formation of alkali-cellulose compounds, the form of the curves is not inconsistent with the view that a series of compounds of the general formula $(C_6H_{10}O_5)_n(NaOH)_m$ may be formed In other words, methods of investigation, capable of much greater accuracy, have yet to be devised The task is not an easy one.

Tests for Mercerised Cotton,

Although cotton is so considerably modified by treatment with strong caustic alkalis, it is often difficult, particularly in the case of technically mercerised and coloured yarns and fabrics, to decide whether or not a sample of cotton has been mercerised The tests which have been proposed all depend on colorimetric methods, so that coloured goods must first be stripped. This must, of course, be accomplished without modifying the properties of the cotton, and this is often a difficult matter Cotton dyed with most direct azo dyes can be stripped with

titanous chloride or sodium hydrosulphite, but Aniline Black and similar fats dyes cannot be so removed

In instances where the cotton cannot be brought to a pure white, evidence of mercerisation can only be obtained by use of the microscope.

When the cotton can be bleached to a pure white condition, the following tests are available

Knaggs (*Journ Soc Dyers & Col.*, 1908, xxiv 112) has suggested the following modified method of Knecht The cotton and some unmercerised cotton is dyed with a solution of Benzo-purpurine 4B (5 c c of a 0·01 per cent. solution of the dye + 100 c c of water), and concentrated hydrochloric acid is then added drop by drop to the boiling liquor (containing the dyed cottons) until the unmercerised cotton changes to blue-black Under these conditions, mercerised cotton will retain its bright red colour

Huebner (*Journ Soc Chem. Ind*, 1908, xxvii 105) has devised a test depending on the fact that mercerised cotton has a greater affinity for iodine than has ordinary cotton. Two solutions are employed one containing 280 g of fused zinc chloride in 300 c c of water and the other containing 1 g of iodine and 20 g of potassium iodide dissolved in 100 c c. of water For use, 0.5 c c of the former solution are added to 100 c c of the latter and the sample of cotton immersed in the mixture for about 20 minutes Mercerised cotton rapidly becomes stained dark blue, while ordinary cotton remains white.

Concentration of Solution (grams of NaOH per 100 grams of Solution).

FIG 41 — PREFERENTIAL ABSORPTION OF CAUSTIC SODA BY COTTON HAIRS AND FABRIC
(Coward and Spencer.)

Huebner also finds that when mercerised and ordinary cotton are immersed for a short period in a 20 per cent. solution of iodine in water saturated with potassium iodide, and are then washed in water, the mercerised cotton remains dark blue, while the ordinary cotton soon loses its colour and becomes white.

It is also evident that mercerisation may also be indicated by methods depending on the greater dyeing power of the cotton (see page 74).

The Lange test, referred to on page 61, consists of immersing cotton in an aqueous solution containing zinc chloride and iodine, and subsequently immersing it in much water. Ordinary cotton soon becomes colourless, but mercerised cotton retains its dark blue colour for a prolonged period, depending on the strength of the caustic soda used in the mercerisation

COTTON AND ACIDS

GENERALLY, cotton is as susceptible to acids as it is resistant to alkalis, and for this reason it is difficult to avoid degradation during any acid treatment   The action of acids, particularly mineral acids, on cotton nearly always results in a loss of strength, and this difficulty has been associated with technical processes of the textile industry from the earliest times

For a considerable number of years, that is since Girard's experiments about 1875 (*Compt rend*, 1875, lxxxi 1105 ; 1879, lxxxviii 1322), cotton weakened (tendered) by treatment with acids has been considered to contain a substance termed hydrocellulose   It is significant, however, that as yet no proof of the chemical identity of such a substance has been obtained.   It is in fact more likely that by such acid treatment no one substance is formed, but rather a number of insoluble compounds more or less nearly related to glucose and certainly less complex than cellulose itself   In this book, therefore, the term hydrocellulose, where used, must be understood to refer to cotton which has suffered partial degradation by treatment with acid and not a chemical compound

Girard was one of the first to investigate the action of mineral and organic acids on cotton.   He showed that aqueous solutions of sulphuric, nitric, hydrochloric and phosphoric acids act with decreasing effect on cotton in the order named.   For instance, Girard found that when cotton was immersed for 12 hours in a solution of sulphuric acid, sp gr 1.453, at ordinary temperature, it retained the normal structure of cotton but lacked strength and was friable   Treatment of cotton for 24 hours with cold hydrochloric acid, sp gr 1.091, yielded a similar product.   Girard considered that cotton treated with mineral acids consisted, or partly consisted, of a substance hydrocellulose and ascribed its formation to a process of hydration, thus

$$\underset{\text{Cellulose}}{C_{12}H_{20}O_{10}} + H_2O \longrightarrow \underset{\text{Hydrocellulose}}{C_{12}H_{22}O_{11}}$$
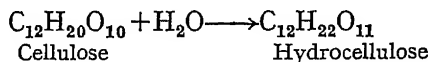
Since Girard's experiments, considerable work has been carried out on the action of acids on cotton and cellulosic materials, and this may be conveniently dealt with according as mineral or organic acids have been employed.

Sulphuric Acid.

Sulphuric acid of all strengths and at all temperatures has action on cellulose. When cotton is placed in cold concentrated sulphuric acid, it rapidly dissolves, becoming dark coloured as the temperature rises. Stern (*Journ. Chem. Soc.*, 1895, lxvii 74) has shown that such a solution contains a cellulose disulphuric ester, $C_6H_8O_3(SO_4H)_2$, and has prepared the corresponding barium, calcium and lead salts.   An aqueous solution of this ester has no reducing action on Fehling's

7

solution and therefore contains no glucose. When heated in the presence of 2 per cent. sulphuric acid, it loses sulphuric acid, forming such compounds as $C_6H_9O_3(SO_4H)$ and $3 C_6H_9O_4 SO_4H$ and then develops reducing power, most probably due to the formation of sugars

Solutions of cotton in sulphuric acid may be quantitatively converted into glucose (see page 185).

The action of concentrated sulphuric acid on cellulose finds industrial application in the treatment of cotton fabrics and paper   For instance, parchmentised paper is obtained by quickly passing the material through cooled sulphuric acid so that the immersion lasts but for a few seconds, and then through water for removal of the acid.   Within recent years, the application of this acid to cotton fabrics has received extended investigation, improvements being discovered and novel effects obtained.

For instance, the action of sulphuric acid is retarded by addition of formaldehyde so that the process may be more easily controlled   In E P 200881 is described a process for parchmentising and crepeing cotton fabrics by treating fabric at 10°–15° C with sulphuric acid of 90°–110° Tw. (sp. gr. 1·45–1·55) containing ½–1 per cent of 40 per cent formaldehyde solution   In E P 196298 the use of certain heterocyclic bases such as pyridine and quinoline are claimed as retarding agents   Thus a soft transparent appearance may be produced on cotton fabric by treating it for 4 minutes at ordinary temperature with a mixture containing 1 part of pyridine and 4 parts of sulphuric acid, sp. gr 1·86   Similarly, a wool-like effect is produced by treatment for 5 minutes with a mixture of 1 part of pyridine and 9 parts of sulphuric acid, sp. gr. 1·66.

The Heberlein Co. have taken out a large number of patents covering the treatment of cotton with sulphuric acid before or after mercerisation with or without tension.   Thus, according to E P 192227, fabric composed of thick cotton yarn may be converted into fabric having a linen-like lustre by mercerising it with caustic soda at —13° C., then treating it for 10 seconds with sulphuric acid of sp gr. 1·535 at 5° C. and afterwards removing the acid by washing.   A wool-like effect is produced by mercerising fabric, treating it with cold sulphuric acid of 49°–51° Tw , washing with water and afterwards mercerising it without tension.

Transparent effects on cotton fabrics are also obtained (E P. 162627) by immersing fabric for 1 to 3 minutes at ordinary temperature in sulphuric acid of 49°–50°·5 Tw. under tension, washing it and afterwards treating it for 3 to 5 seconds at ordinary temperature with sulphuric acid of 52°–54° Tw. and then mercerising it with caustic soda of 30°–40° Tw.

In some processes, sulphuric acid containing nitric acid is employed.   For instance, according to E P. 167864, a transparent effect is produced on cotton by treating it at 10° C. with a mixture of equal volumes of sulphuric acid, sp gr 1·652, and nitric acid, sp. gr. 1·397, for 10 seconds.   When the treatment is extended for 40 seconds and a mixture of equal volumes of sulphuric acid, sp gr. 1·643, and nitric acid, sp. gr. 1·383, is employed, a wool-like effect is obtained.

When cotton is subjected to the action of dilute sulphuric acid, the most important effect is one of tendering, combined with an increased activity towards alkalis and strong acids (e g nitration)

Stern (*Journ Chem Soc*, 1904, lxxxv. 336) found that cotton suffered a loss in weight of 2–4 per cent , and was reduced to a friable powder when boiled with 5 per cent sulphuric acid   Scheurer and Koechlin (Worden) found cotton to be appreciably tendered when immersed for 30 minutes in 0 2 per cent. sulphuric acid at 80° C , and a measurable amount of tendering occurred when Coward, Wood and Barrett (*Journ Text Inst*, 1923, xiv 523) treated cotton for 1 hour with boiling 0·05 per cent sulphuric acid

Halogen Acids.

Hydrochloric acid converts cellulose into simpler substances, such as sugars and dextrins, in much the same manner as does sulphuric acid, but no evidence exists to show that cellulose combines with hydrochloric acid

When cotton is immersed in cold concentrated hydrochloric acid (37–38 per cent) it suffers slow degradation   On the other hand, Willstatter and Zech-meister (*Ber*, 1913, xlvi 2401) found that when cold acid containing 41–42 per cent HCl (obtained by passing dry hydrochloric acid gas into cooled concentrated aqueous hydrochloric acid) is used, the cotton dissolves within about 10 seconds to form a clear solution   With hydrochloric acid solutions of sp gr 1·204, 1·209 and 1·212, clear solutions containing 7, 12–13 and 15 per cent of cotton were prepared   Such solutions, though clear at first, yield a slight flocculent precipitate at the end of one day, and afterwards become yellow in colour and form a dark brown insoluble substance.

When a freshly prepared solution of cotton is diluted with water, a form of cellulose is precipitated quantitatively, for the filtrate even after prolonged boiling has no reducing action with Fehling's solution   A cotton solution undergoes hydrolysis on standing since it acquires reducing powers.   Willstatter and Zechmeister (see page 185) assumed that the cellulose was thus converted into glucose only, and on this assumption and by means of a polarimeter and analyses with Fehling's solutions, were able to show that this conversion was almost quantitative (95–96 per cent)

Lignin substances were found to be insoluble in these highly concentrated solutions of hydrochloric acid, and on this basis Willstatter and Zechmeister devised a method of estimating the cellulose content of wood and other fibrous materials.

Knoevenagel and Busch (*Cellulosechem*, 1922, iii 42) observe that cellulose and particularly slightly modified forms such as that regenerated from viscose and cellulose acetate, when placed in a closed vessel containing dry hydrogen chloride gas, absorbs this gas in proportion to its moisture content.   According to the conditions, a product can be obtained which is completely soluble in 8 per cent. caustic soda and which is quantitatively precipitated from such solution

by addition of acid. In the case of viscose cellulose, the change is brought about within two hours, and the alkali soluble cellulose thereby produced has a high copper number of about 12·5–14·0, and readily forms a tribenzoate completely soluble in chloroform.

Although cellulose is not easily dissolved by ordinary concentrated hydrochloric acid, Ostenberg (Worden) has observed that solution readily takes place at —10° to —15° C. in 35 per cent hydrochloric acid, to which 8–10 per cent. of concentrated sulphuric acid has been added.

Vignon (quoted by Worden) has found that when cotton is immersed in hydrochloric or sulphuric acid there is an evolution of heat, thus

TABLE XLV

Acid	Heat Developed	
	100 g of Bleached Yarn	100 g of Bleached Loose Cotton
Sulphuric acid	0·40 cals.	0·40 cals
Hydrochloric acid . . .	0·38 ,,	0·36 ,,

Concentrated hydriodic acid does not dissolve cotton in the cold, but a 66 per cent solution hydrobromic acid does so readily and completely even at 0° C. Similarly, cellulose is soluble in 66 per cent. hydrobromic acid, but only incompletely in 57 per cent. acid From this solution, the cellulose can be recovered quantitatively by precipitation immediately after solution is complete.

Hydrofluoric acid of 70–75 per cent. dissolves cotton, but at lower strengths solution is only effected with degradation of the cotton

It has been stated (U S.P. 763473/1904) that aqueous solutions of sulphur dioxide at 120°–160° C. dissolve cellulose

Concentrated solutions of phosphoric and arsenic acids slowly dissolve cotton in the cold, but these facts have not been thoroughly investigated or received technical application. Deming (*Journ. Amer. Chem. Soc*, 1911, xxxiii. 1515) observes that cotton is soluble in cold and readily soluble in hot syrupy arsenic acid ; also that hot selenic acid is a solvent for cellulose.

Nitric Acid.

The action of nitric acid on cellulose differs from that of other mineral acids since it has distinct oxidising properties. When cotton is treated with hot

dilute nitric acid, it is oxidised and ultimately hydrolysed to sugar substances, and this action will therefore be referred to in Chapter VI (see page 148).

It has long been known, however, that by means of concentrated nitric acid, cellulose nitrates may be formed which under ordinary conditions are stable. Schonbein indicated in 1845 the general method by which such compounds of cellulose may be prepared, the nitrating agent most suitable being a mixture of nitric and sulphuric acids. There is evidence that the following nitrocelluloses have been prepared, but in most instances the product of nitration consists of a mixture of these nitrates, since the nitrogen content may be varied continuously by alteration of the conditions of nitration.

TABLE XLVI

Nitrocellulose.			Formula	Nitrogen Content
Dodeca-nitrocellulose	.	.	$C_{24}H_{28}O_8(NO_3)_{12}$	14·2 per cent
Endeca-nitrocellulose	.	.	$C_{24}H_{29}O_9(NO_3)_{11}$	13·5 ,,
Deca-nitrocellulose	.	.	$C_{24}H_{30}O_{10}(NO_3)_{10}$	12·8 ,,
Nono-nitrocellulose	.	.	$C_{24}H_{31}O_{11}(NO_3)_9$	11 9 ,,
Octo-nitrocellulose	.	.	$C_{24}H_{32}O_{12}(NO_3)_8$	11·1 ,,
Hepta-nitrocellulose	.	.	$C_{24}H_{33}O_{13}(NO_3)_7$	10·2 ,,
Hexa-nitrocellulose	.	.	$C_{24}H_{34}O_{14}(NO_3)_6$	9 1 ,,
Penta-nitrocellulose	.	.	$C_{24}H_{35}O_{15}(NO_3)_5$	8 0 ,,
Tetra-nitrocellulose	.	.	$C_{24}H_{36}O_{16}(NO_3)_4$	6·8 ,,
Tri-nitrocellulose	.	.	$C_{24}H_{37}O_{17}(NO_3)_3$	5·4 ,,
Di-nitrocellulose	.	.	$C_{24}H_{38}O_{18}(NO_3)_2$	3·8 ,,
Mono-nitrocellulose	.	.	$C_{24}H_{39}O_{19}(NO_3)_1$	2·0 ,,
Cellulose	.	.	$C_{24}H_{40}O_{20}$	..

All nitrocelluloses are fibrous in nature and readily inflammable. Under suitable conditions, they may be used as explosives, for the preparation of lacquers, celluloid films and artificial silk.

For use as an explosive, guncotton, the most highly nitrated cotton, is employed. It is prepared by treating purified cotton waste with about thirty times its weight of a mixed acid containing (Worden) 75·00 per cent. of sulphuric acid, 15·75 per cent. of nitric acid, 1·30 per cent. of nitrous acid and 7·95 per cent of water, at 15° C. The temperature during the reaction rises to about 25° C. and finally falls to about 20° C., and the nitration may take about 12 hours. Afterwards, the nitrated cotton is washed with cold water and then further purified with boiling water.

Guncotton contains about 13 per cent. of nitrogen and is practically insoluble in alcohol-ether. It is soluble in acetone and ethylacetate but only partly soluble in amylacetate.

Pyroxlin is a less highly nitrated cotton containing about 12·3 per cent. of nitrogen, and is readily soluble in amyl or ethylacetate, acetone and methylethyl ketone. It is prepared by the action at 45°–55° C. of a mixed acid containing

55 per cent. of sulphuric acid, 17 per cent. of nitric acid and 28 per cent. of water on cotton. This nitrocellulose was first used by Chardonnet for the manufacture of artificial silk (see page 192). According to Worden, pyroxylin is the name given to all nitrocelluloses completely soluble in amylacetate and in commercial wood alcohol

Nitrocellulose, suitable for the preparation of photographic films, contains $11 \cdot 5$–$12 \cdot 5$ per cent of nitrogen and is soluble in alcohol-ether and in wood alcohol For the manufacture of celluloid, nitrocelluloses of low nitrogen content—$10 \cdot 7$ per cent.—are employed together with camphor or camphor substitutes

Although mercerisation with caustic soda is generally adopted as a means for increasing the lustre of cotton, this result may also be obtained by means of nitric acid Knecht states (*Journ Soc Dyers & Col*, 1896, xii. 89) that when cotton is steeped for a few minutes in nitric acid of 83° Tw. (sp. gr $1 \cdot 415$) it becomes gelatinous, but when afterwards washed with water, it is found to have shrunk, gained in strength and possesses an increased affinity for direct dyestuffs ; it also has an increased lustre Nitric acid of 77° Tw (sp. gr. $1 \cdot 385$) does not produce this effect

Subsequently Knecht (*ibid*, 1904, xx. 68) found that when cotton was steeped for about 6 hours in nitric acid of 84° Tw. (sp gr $1 \cdot 420$) it acquires an affinity for acid dyestuffs such as Acid Violet, Naphthol Yellow and Crystal Scarlet More recently (*Dyer & Calico Printer*, 1924, li. 56) Budnikow has continued these investigations, and obtained the following results when cotton yarn was treated with nitric acid of 40°–41° Bé (sp gr $1 \cdot 38$–$1 \cdot 39$) at 10°–15° C.

TABLE XLVII

Duration of Treatment	Strength of Treated Yarn	Elongation of Treated Yarn.
Nil . . .	33 5 kg	5 2 per cent
5 seconds	34·5	7 5 ,,
10 ,, . .	34·4	7 6 ,,
15 ,, . .	37·2	7 6 ,,
25 ,,	39·3	7·9 ,,
30 ,, . .	40 4	7·9 ,,
45 ,,	38 8	8 2 ,,
1 minute . .	38·1	8·4 ,,
1·5 ,, .	36·8	8·6 ,,
2 minutes . .	36 2	8·6 ,,
5 ,, .	35·1	8·5 ,,
7 ,, . .	34·1	8·7 ,,
12 ,, .	33 6	8·9 ,,
15 ,, .	31 7	9·3 ,,
25 ,, . .	30 1	9 1 ,,
1 hour . .	29·1	9 0 ,,
2 hours . .	24 2	8·3 ,,
8 ,,	6 2	4 0 ,,
22 ,, . .	6 0	4·0 ,,

It is therefore concluded that the treatment is most satisfactorily effected at ordinary temperature for 15–30 seconds   After such treatment, cotton fibres lose much of their twist, swell and the cuticle thereby becomes smooth and transparent   The inner canal also becomes contracted, and the lustre is increased. Cotton so treated has an increased affinity for acid dyes and for direct, vat and other classes of dyestuffs

Organic Acids.

In recent years, the action of organic acids on cotton has been extensively investigated, and many cellulose esters of such acids have been prepared and in the case of the acetates largely used for technical purposes   Generally, however, organic acids react much less drastically than mineral acids on cellulose, and for this reason, such acids as acetic, formic, oxalic and lactic acids are largely used in technical processes of bleaching and dyeing when tendering of fabrics and yarns is undesirable

Formic Acid.

Dilute solutions of formic acid may be dried up in cotton without appreciable tendering, but stronger acids attack cellulose with formation of esters   Cotton is not soluble in concentrated formic acid, but it readily dissolves when sulphuric acid or zinc chloride is also present

Cellulose which has been previously treated with acids is more soluble in formic acid than ordinary cotton

It does not appear that pure cellulose formates have been prepared, but they have been shown to exist in mixtures   Beryl and Smith have prepared a mixture of mono- and di-formates (*Ber*, 1907, xl 903), thus :

6·5 g of hydrocellulose prepared by the method of Girard (see page 89) was allowed to stand at ordinary temperature with 100 g of anhydrous formic acid and 5 c c of concentrated sulphuric acid   After 4 days, the cotton was completely gelatinised and the product was then treated with water in order to remove excess of acid   The residual insoluble cellulose formate was found to contain 20 23 per cent of formic acid and was soluble in acetone, chloroform, and partly soluble in pyridine   It was not soluble in alcohol-ether

A later method for preparing cellulose formates (E P 2511 of 1911) consists of treating 15–30 parts of cotton with 100 parts of 98 per cent formic acid and 2–4 parts of dry hydrochloric acid at 15°–18° C   The cotton dissolves in about 24 hours and the formate is freed from excess of acids in the usual manner   The cellulose formate thus obtained is stated to be soluble in formic and acetic acids

Acetic Acid.

The action of acetic acid on cellulose has become of great importance in consequence of the technical importance of cellulose acetates as a basis for the

manufacture of artificial silk and films and dope (a protective composition for use on aeroplane fabrics). These technical products are described later (see Chapter IX.).

In early investigations, some difficulty was experienced in securing a reaction between cotton and acetic acid, and it was not until catalysts were employed that cellulose acetates could be obtained   It is now found that cotton readily reacts with a mixture of acetic anhydride, glacial acetic acid and a catalyst such as zinc chloride, phosphoric acid, chloracetic acid and dimethyl sulphate, etc. For instance, when cotton is immersed in a mixture of 50 parts of acetic anhydride, 50 parts of glacial acetic acid and 4–6 parts of sulphuric acid, it is rapidly dissolved at $30°$–$40°$ C and forms the compound—$(4C_6H_7O)SO_4(C_2H_3O_2)_{10}$ A disadvantage of these catalysts, however, is that they result in degradation of the cellulose ester as it is formed, and they may also affect the transparency and flexibility of films and threads made from the resulting cellulose acetate.

Ost (*Zeit. angew. Chem*, 1919, xxxii. 66, 76 and 82) considers that zinc chloride is the catalyst which results in the least degradation of the cellulose and prepares cellulose triacetate thus ·

100 g. of cotton are gradually added to a mixture consisting of 400 g of acetic acid, 400 g. of acetic anhydride and 100 g. of fused zinc chloride   Heat is developed and the mixture is cooled below $40°$ C.   The resulting syrup is then poured into water whereby cellulose triacetate is precipitated and may be freed from acids and zinc salts by washing.

Sulphuryl chloride has also been found useful as a catalyst (E P 24382 of 1910), but recently Barnett (*Journ. Soc. Chem. Ind.*, 1921, xl. 8) has indicated a method by which cellulose acetates may be obtained with the minimum amount of degradation of the cellulose   Barnett has found that if cellulose is treated with a suitable mixture of glacial acetic acid, acetic anhydride and a trace of chlorine, no acetylation occurs unless the mixture is heated for a considerable time. Similarly, if the chlorine is substituted by sulphur dioxide, acetylation takes place to an even smaller extent   If, however, traces of both chlorine and sulphur dioxide are present, acetylation proceeds rapidly and a colourless jelly of cellulose acetate dissolved in the excess of acetic acid is obtained

Thus, in one experiment, 200 g. of glacial acetic acid, containing just sufficient chlorine to colour it, was poured on 50 g of filter paper.   After standing for some time, 250 g. of acetic anhydride was added and a few bubbles of sulphur dioxide passed through the mixture   The temperature at once increased, and when maintained at $65°$ C. by cooling, a clear solution of cellulose diacetate was obtained within one hour.   After standing overnight, the cellulose diacetate was separated in the form of a white powder, soluble in acetone, chloroform, pyridine, hot nitrobenzene, aniline and slightly soluble in a mixture of alcohol and benzene

In another experiment, 5 g of filter paper was immersed in 20 c c of glacial acetic acid, and 20 c.c. of acetic anhydride, containing 0 32 g of chlorine, added

Then 2 c c. of acetic anhydride containing 0·26 g. of sulphur dioxide were further added, whereby the mixture rapidly gelatinised and solution was complete within 5 minutes From the product, white flakes of cellulose triacetate were separated.

It was observed that acetylation proceeded most satisfactorily when the weights of chlorine and sulphur dioxide were approximately in the ratio of their molecular weights—corresponding to the formation of sulphuryl chloride SO_2Cl_2 *in situ*. Further, the product depends on the conditions of acetylation If the temperature is maintained below 65° C. and only a trace of sulphur dioxide be employed, the product is chiefly cellulose diacetate If the temperature is allowed to exceed 65° C. and the ratio of chlorine to sulphur dioxide is nearer to unity, then the product is mainly cellulose triacetate Cellulose acetates prepared by these methods do not darken or lose their valuable physical properties (*e g* strength, flexibility, etc) when heated at 100° C. for several days

The direct formation of cellulose monoacetate by direct acetylation does not yet appear possible, but Grun and Wittka (*Zeit. angew. Chem* , 1922, xxxiv. 645) indicate that the monoacetate can be produced by the action of alcohol on cellulose triacetate, whereby ethylacetate is formed as a by-product Cellulose diacetate can be similarly prepared from cellulose triacetate by hydrolysis

All the cellulose acetates yet produced are amorphous white substances which have varying solubilities in different organic solvents, and from which they may be regenerated in the form of masses, films or threads. They are, however, all soluble in hot nitrobenzene

In a later investigation Barnett (*Journ Soc Chem Ind* , 1921, xl 253) has shown that cotton is vigorously attacked under various conditions with chloro-acetyl chloride, dichloroacetyl chloride and mixtures of these with acetic anhydride The reaction in most instances can only be controlled when an inert diluent such as benzene, toluene or pyridine is present. Thus, when chloro-acetyl chloride is allowed to react with cotton in the presence of alkalis and little or no water is present, a violent reaction occurs and the cellulose becomes charred. In some instances, the resulting products contain combined chlorine

Oxalic Acid.

Aqueous solutions of oxalic, tartaric and citric acids have little effect on cotton except on prolonged boiling, although Scheurer (*Journ Soc Dyers & Col* , 1893, ix 206 , 1901, xvii 156) has observed tendering when cotton fabric containing these acids is steamed An observation (*Dyer & Calico Printer*, 1902, p. 91) on further investigation by Knecht (*Journ Soc Dyers & Col* , 1907, xxiii 231) showed that when oxalic acid is dried in cotton fabric, the oxalic acid decomposes into carbonic and formic acids, the latter then forming an ester with the cellulose. This ester is readily saponified with caustic soda, normal cellulose being regenerated

Briggs (*Journ Soc Chem. Ind* , 1912, xxxi 520) in the examination of fabric tendered by oxalic acid also concludes that oxalic acid can form an ester with

cellulose.   Among some pieces of linen fabric over which some oxalic acid had been spilled and which had lain in a warehouse for over one year, Briggs found one which when spotted with a solution of methyl orange reacted acidic, but whose aqueous extract was neutral and contained no oxalates   The same fabric was definitely tendered   When, however, the fabric was boiled with an alkali, the extract was shown to contain an oxalate.   These facts suggested that oxalic acid was capable of uniting with cellulose to form a neutral ester, and this was then confirmed.

Fabric impregnated with a 5 per cent solution of oxalic acid was heated for 30 hours at 45°–50° C., and it was then shown that the cellulose combined with 1 per cent. of its weight of the acid.   Under similar conditions, using a 10 per cent solution of oxalic acid, cellulose combined with 2·3 per cent of the acid, but if the heating was carried out for 24 hours at 95° C., then 3·7 per cent of acid was fixed.

When strips of cotton were dipped in a fused mixture containing 20 g of oxalic acid and 5 c.c of water, and afterwards heated for 4 days at 95° C , the strips became tender and contained 6 4 per cent of combined oxalic acid

Heuser and Eisenring (Cellulosechem , 1923, iv 25) have recorded that when cellulose, regenerated from solutions of viscose, was heated in a sealed tube at 100° C. for 2½–12 hours with 8–16 per cent solutions of oxalic acid, an insoluble hydrocellulose product was obtained having copper numbers (see page 136) of 10·47–10·83.   When a 5 per cent solution of oxalic acid was employed and the temperature was raised to 180° C., the yield of insoluble product was considerably diminished and dextrose was found in solution   The insoluble products were completely soluble in 8 per cent. caustic soda.   Similar results were obtained with cotton-cellulose, but the insoluble products were only partially soluble in 10 per cent caustic soda.   Cotton-cellulose heated at 180° C for ½ hour with 5 per cent. oxalic acid yielded 0·81 per cent of w-hydroxymethylfurfuraldehyde, whereas 11·86 per cent and 5·74 per cent. of this substance were obtained from hydro-cellulose produced from viscose cellulose and from cellulose respectively

Various Organic Acids.

Cellulose di-stearate and cellulose di-laurate have been prepared by Grun and Wittka (Zeit. angew. Chem , 1921, xxxiv. 645) by a general method in which cotton is treated with the acid chloride of the fatty acid in the presence of pyridine or benzene.   These esters retain the fibrous structure of cotton, and though insoluble in cuprammonium solution are soluble at about 200° C in fatty acids and glycerol

Cellulose di-stearate forms white fibres, m p 220° C (decomp), and the di-laurate is a similar product, m p. 250° C

The characteristic property of cellulose esters by which they exchange esterifying groups when heated with an aliphatic alcohol is less evident in the case of the di-laurate and di-stearate of cellulose, indicating that the stability
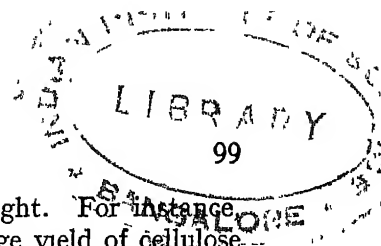
of cellulose esters increases with the greater molecular weight. For instance, when cellulose triacetate is heated with ethyl alcohol, a large yield of cellulose-monoacetate is obtained, but under similar conditions only a small proportion of stearic acid is removed from cellulose di-stearate.

Gault and Ehrmann (*Compt rend*, 1923, clxxvii 124) have shown that hydro-cellulose is readily converted into esters (di-palmitic, di-stearic and di-lauric) which are insoluble in water, alcohol and acetone, but soluble in most other organic solvents, by heating it at 110°–120° C for 2–3 hours with five times its weight of an acid chloride in the presence of pyridine

Cellulose hexa-palmitate, $C_{12}H_{14}O_{10}(CO\ C_{15}H_{31})_6$, was prepared by Karrer, Peyer and Zorka Zega (*Helv Chim Acta*, 1922, v 853) by the action of palmityl chloride on cellulose in the presence of quinoline   It is a white amorphous substance having m p. 78° C

Cellulose hexa-stearate, $C_{12}H_{14}O_{10}(CO\ C_{17}H_{35})_6$, a slightly yellow powder having m p 83°–118° C , has been prepared in a similar manner using stearyl chloride

According to Gomberg and Buchler (*Journ Amer Chem Soc*, 1921, xliii. 1904), cellulose, particularly hydrocellulose, is readily converted into mono-, tri- and tetra-benzyl derivatives by heating it at 90° C with benzyl chloride and aqueous caustic soda.

A recent process for preparing cellulose butyrate (E P. 167143) consists of impregnating cellulose with about 1½ times its weight of 90 per cent acetic acid containing sulphuric acid, and then heating it in a mixture of about equal parts of butyric acid and butyric anhydride.   Heat is developed during the reaction (the sulphuric acid acts as a catalyst), and cellulose butyrate, soluble in chloroform, acetone, hot alcohol, benzene and phenol, is produced

The preparation and properties of cellulose phthalate, $C_8H_4O_3\ 8C_6H_{10}O_5\ 4H_2O$, are described by Levey (*Journ Ind Eng. Chem.*, 1920, xii 743)   It is preferably prepared from hydrocellulose by heating this for 24 hours at 70° C. with phthalic anhydride and zinc chloride together with acetic acid   It was found to be insoluble in most organic solvents   Phthalic anhydride is not capable of replacing the acetate radicles present in cellulose triacetate.

Cellulose esters of benzoic acid may be obtained by the action of benzoyl chloride on cotton or hydro-cellulose (Cross, Bevan and Briggs—*Zeit. angew. Chem*, 1913, xxvi 255 ; Ost and Klein—*ibid*, 437).   The esters may also be produced by means of the Schotten-Baumann reaction in which alkali-cellulose —$C_6H_{10}O_5$ NaOH—is treated with benzoyl chloride, thus

$$C_6H_{10}O_5 + NaOH + C_6H_5COCl = C_6H_9O\ CO\ C_6H_5 + NaCl + H_2O$$
<div align="center">Cellulose-mono-benzoate.</div>
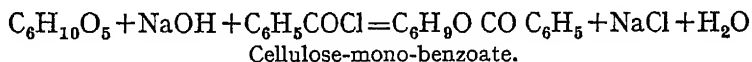
In this manner, cellulose mono-, di- and tri-benzoates may be prepared with but little modification of the cellulose.   They are amorphous or fibrous white solids soluble to a varying extent in organic solvents and are capable of saponification It is likely that they will find technical use in the future

Tannic Acid.

For many years the affinity of tannic acid for cotton has been known and employed in dyeing   It is found that when cotton is steeped in aqueous solutions of this substance, it is absorbed by the cotton so strongly that on prolonged washing with cold water, only a part of the tannic acid is removed   The absorbed tannic acid is, however, largely removed by treating the cotton with boiling water.

Knecht and Kershaw (*Journ. Soc Dyers & Col*, 1892, viii 40) have recorded the following results .

5 g of cotton were immersed in 150 c c. of water containing 5 per cent. of tannic acid (calculated on the weight of cotton) for different periods at different temperatures and the absorption of tannic acid, determined in the following instances

1. The cotton was steeped cold for 3 hours
2 The cotton was entered boiling and allowed to cool during 3 hours.
3 The cotton was steeped at 50° C for 3 hours
4 The cotton was steeped boiling for 1 hour

It was then found—

TABLE XLVIII

Experiment	Tannic Acid absorbed by Cotton	Tannic Acid remaining in Solution
1	0 0363 g.	0·2137 g.
2	0·0513	0 1987
3	0·0082	0·2418
4	0·0025	0·2475

In another experiment, cotton was entered in a boiling solution of tannic acid (concentration as above described) and allowed to cool overnight. The absorption was observed to be .

Tannic Acid absorbed by Cotton	Tannic Acid remaining in Solution
0·0612 g	0·1888 g

Afterwards, 5 g samples of this cotton were

1. Steeped in cold water (150 c c) for 1 hour ,
2. Steeped in cold water (150 c c) for 3 hours ,
3 Steeped in boiling water for 1 hour ,

and the tannic acid removed from the cotton was shown to be

TABLE XLIX

Experiment	Tannic Acid retained by Cotton	Tannic Acid removed
1	0 0465 g.	0 0147 g
2	0·0393	0·0221
3	Nil.	0 0612

Cotton containing (mordanted with) tannic acid has the power of absorbing and retaining basic dyestuffs, and cotton is largely treated for this purpose   Since, however, it is found that the resulting dyeings are faster to washing if the tannic acid is also fixed within the cotton by treating it with a solution of an antimony salt, such as tartar emetic, this operation is almost always carried out by dyers.

Gardiner and Carter (*Journ Soc Dyers & Col* , 1898, xiv 143) found that regenerated cellulose has a greater affinity for tannic acid than has ordinary cotton, and also that the absorption of tannic acid from aqueous solution by cotton is largely influenced by the presence of other acids

Thus 10 g samples of cotton were immersed in 1000 c c of aqueous solutions containing 1 g. of tannic acid and various other acids, the absorption of tannic acid by the cotton being determined in the following instances
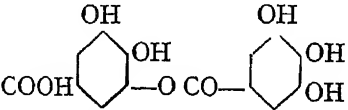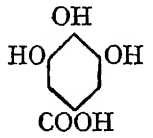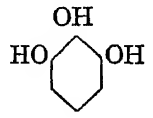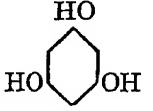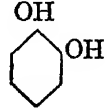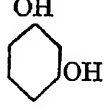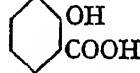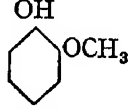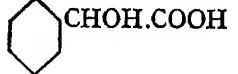
TABLE L

Tannic Acid Solution, containing .		Tannic Acid absorbed by Cotton			
o per cent of acetic acid	. .	30–32 per cent of total amount present			
1 ,, ,,	. . .	35–36	,,	,,	,,
2 ,, ,,	. . .	40–42	,,	,,	,,
5 ,, ,,	. . .	49–51	,,	,,	,,
10 ,, ,,	. . .	32–43	,,	,,	,,
20 ,, ,,	. . .	31–32	,,	,,	,,
10 per cent of acetic acid	. .	48–50	,,	,,	,,
,, citric acid	. .	19–21	,,	,,	,,
,, tartaric acid	. .	20–22	,,	,,	,,
,, sulphuric acid	. .	18–20	,,	,,	,,
,, hydrochloric acid .	.	32–30	,,	,,	,,
,, sodium acetate	. .	16–18	,,	,,	,,

It is also found that cotton has no affinity for gallic acid, and these workers therefore compared the affinity of cotton for various compounds related to tannic

acid   The method consisted of immersing 10 g. of cotton in 1000 c c. of water containing 1 g. of the substance and determining the amount of substance remaining in aqueous solution.   The following results were obtained :

TABLE LI

Substance	Percentage of Total Amount of Substance absorbed
Gallotannic acid	30–32 per cent
Gallic acid	0 ,,
Pyrogallol	4 5 ,,
Phloroglucinol	24–26 ,,
Catechol	0 ,,
Resorcinol	45–50 ,,
Salicylic acid	0 ,,
Guiacol	0 ,,
Mandelic acid	7–8 ,,

Absorption by cotton of such a substance therefore appears likely if it contains, in the meta positions, either two hydroxyl groups or hydroxyl and carboxylic acid groups

It may here be incidentally noted, that Katanol has now been placed on the market as a satisfactory substitute for tannic acid   Katanol consists of sulphurised phenols (U S P. 1450463/21) for which cotton has a good affinity, and the cotton mordanted with this substance has a strong affinity for basic dyes   This substance has the advantage that cotton treated with it does not require further fixing with antimony salts

Tendering of Cotton with Acids.

In technical practice tendering is of considerable importance and, as may be expected, much work has been done relating to the loss of strength produced by the treatment of cotton hairs, yarns and fabrics with various acids, without particular reference to the chemical nature of the treated cotton

Fort and Pickles (*Journ Soc Dyers & Col.*, 1915, xxxi 255) put forward evidence to show that the tendering of cotton by acids is mainly dependent on the concentration of the hydrogen ion, in much the same manner as is the hydrolysis of cane sugar by acids   These workers immersed 5 g samples of cotton yarn in 100 c c of boiling acid heated on a boiling water bath for 60 minutes, the yarn being afterwards washed and dried at 40°–50° C. The yarn was subsequently tested for tensile strength, and the following results were obtained :

TABLE LII

Acid	Strength of Acid as measured by Electrical Conductivity.	Percentage Loss of Strength of Yarn.
N/1 Hydrochloric acid . .	100	100
N/1 Sulphuric acid . . .	65·1	$\begin{cases} 93 \cdot 0 \\ 93\ 7 \end{cases}$
N/1 Oxalic acid . .	19·7	$\begin{cases} 69 \cdot 2 \\ 73 \cdot 1 \end{cases}$
N/1 Acetic acid . .	0 4	$\begin{cases} 11 \cdot 2 \\ 10 \cdot 6 \end{cases}$
N/1 Sodium bisulphate . .	..	$\begin{cases} 54\ 9 \\ 50 \cdot 9 \end{cases}$
2N Oxalic acid . . .	19 7	72·7
2N Phosphoric acid (H_3PO_4) .	7·3	36·8
2N Monochloroacetic acid .	4·9	42·0
2N Tartaric acid . . .	2·3	34·4
2N Formic acid . . .	1·7	19·7
2N Acetic acid . . .	0·4	17·1
Water	..	$\begin{cases} 3 \cdot 2 \\ 5 \cdot 8 \end{cases}$

Similar evidence has been obtained by Coward, Wood and Barrett (*Journ. Text Inst.*, 1923, xiv. 520) in respect of bleached cotton fabric   Samples of the fabric were immersed in solutions of various acids at different temperatures for definite periods of time, and were then thoroughly washed, air dried and subsequently tested for strength in a Goodbrand machine with strips 2 inches wide and 6 inches long between the jaws   The following results were obtained

TABLE LIII

PERCENTAGE TENDERING AT 100° C.

Acid.		2N Acid			N Acid.			N/10 Acid		
Time in minutes	1.	15	60	1	15	60	1.	15	60
Hydrochloric acid	100	100	100	100	100	100	9	54	100
Sulphuric acid	22	100	100	34	100	100	12	32	32
Hydrofluoric acid	11	100	100	7	28	51	0	11	31
Acetic acid	0	15	15	4	9	18	..	5	14
Monochloracetic acid	3	35	100	17	23	39	0	0	16
Trichloroacetic acid	..	..	.	5	84	100	..	..	11
HCl+NaCl	100	100	100	100	100	100	12	34	100
KHF	0	0	0	0	0	0	0	0	0
KHSO₄	..	..	..	..	..	.	..	..	55

TABLE LIV

PERCENTAGE TENDERING AT 60° C.

Acid.		2N Acid			N Acid			N/10 Acid		
Time in minutes	1.	15	60	1	15	60	1.	15	60.
Hydrochloric acid	16	45	100	7	25	52	.	0	0
Sulphuric acid	9	16	66	14	18	25	0	0	5
Hydrofluoric acid	0	0	0	0	0	0	0	0	0
Acetic acid	..	2	0	..	0	0	0	0	0
Monochloracetic acid	0	7	12	..	.	7	..	..	0
Trichloracetic acid	..	..	..	..	20	36	..	..	..
HCl+NaCl	5	61	100	0	13	50	..	..	..
KHSO₄	2	0	25	0	0	2	..	..	..

Measurable tendering was observed when cotton was treated for 1 hour with N/100 sulphuric acid at 100° C.

In the above results it is evident that the degree of tendering is largely determined by the relative strength of the acid, and the following results illustrate clearly this general relationship. The cotton fabric was treated for 1 hour at 60° C.

TABLE LV

Acid	Strength of Acid in Normal Solution.	Percentage Tendering
Hydrochloric acid . . .	0·88 Normal	52 per cent
Trichloracetic acid [1] . .	0 65 ,,	36 ,,
Sulphuric acid . . .	0·57 ,,	25 ,,
Hydrofluoric acid . . .	0·13 ,,	0 ,,
Monochloracetic acid . .	0 05 ,,	7 ,,
Acetic acid	0·006 ,,	0 ,,

[1] Liable to produce hydrochloric acid by hydrolysis

These same workers found that perfectly dry hydrogen chloride gas only produced a tendering of 18 per cent when allowed to act for 2 hours at 15° C. on dry cotton, thus confirming the observations of Girard (*Ann Chim Phys*, 1881, xxiv. 361) In the presence of a little moisture, tendering was instantaneously produced Under similar conditions, but at 100° C, dry hydrochloric acid caused the cotton to become brown and tender, but when sulphurous dioxide was employed at the same temperature, the tendering produced within 2 hours was only 17 per cent.

Solutions of hydrochloric acid gas in ether, alcohol and benzene were found to be more injurious to cotton than similar aqueous solutions

Cohen (*Journ. Soc Dyers & Col*, 1915, xxxi 162) endeavoured to co-relate the loss of strength and the copper number of cotton yarn which has been subjected to the action of acids The following results indicate that with increasing strength of acid, the copper number and loss of strength of the cotton become higher. They were obtained after boiling cotton with sulphuric acid for 1 hour.

TABLE LVI

Strength of Acid	Tensile Strength	Copper Number.
1 000 per cent.	220	2·50
0·500 ,,	340	1·80
0 250 ,,	390	1 30
0·125 ,,	440	1·00
0 067 ,,	495	0·77
0 033 ,,	535	0 61
0·000 ,,	575	0·84

8

In technical practice, cotton materials are frequently tendered because they are dried while containing small amounts of acid   The higher the temperature of drying, the greater the amount of tendering.   It is therefore useful to know the maximum amount of acid which may safely be allowed to remain in fabrics during drying

Lester (*Journ Soc Chem Ind.*, 1915, xxxiv 934) considers that 0·01 per cent of hydrochloric acid (calculated on the weight of cotton) is the maximum limit Thus he impregnated fabric with 0 01 per cent and 0 10 per cent of hydrochloric acid and found the amount of tendering after drying with a hot iron and (*b*) when subsequently heated for 1½ hours in a water oven, to be as follows

TABLE LVII

Strength of Acid.	Breaking Strain	
	(*a*)	(*b*)
Nil	105	95
0·01 per cent	100	92
0·10 ,,	90	13

Coward, Wood and Barrett (*Journ Text Inst*, 1923, xiv 520) have carried out investigations on similar lines with grey, desized grey and bleached cotton fabric   Samples of fabric were impregnated with an acid solution and then dried for 10 minutes between two electrically-heated copper plates at 100° C and 120° C, during which time they became quite dry   Subsequently, the dried fabric was well washed in water and air-dried and tested for loss of tensile strength The results are shown in Figs 42 and 43   It is evident that fabric impregnated with its own weight of a 0·05 per cent solution of hydrochloric acid is badly tendered when dried at 100° C, and when dried at 120° C a 0 01 per cent solution is sufficient to produce tendering.

Some interesting facts concerning the tendering of cotton by drying while containing sulphuric acid have been observed by Knecht and Thompson (*Journ Soc Dyers & Col*, 1921, xxxvii 270)   These workers find that cotton tendered by immersion in warm or hot acid solutions has distinctly different properties from that tendered by drying-up with sulphuric acid   Thus when cotton is boiled for ½ hour in 0 5 per cent sulphuric acid, it loses strength, but after washing it contains no sulphur and has a slightly decreased affinity for Methylene Blue On the other hand, cotton dried up with a similar acid contains combined sulphur and has an increased affinity for Methylene Blue   When cotton was dried for 2 hours at 40°–45° C. with 2N sulphuric acid, afterwards washed in water,
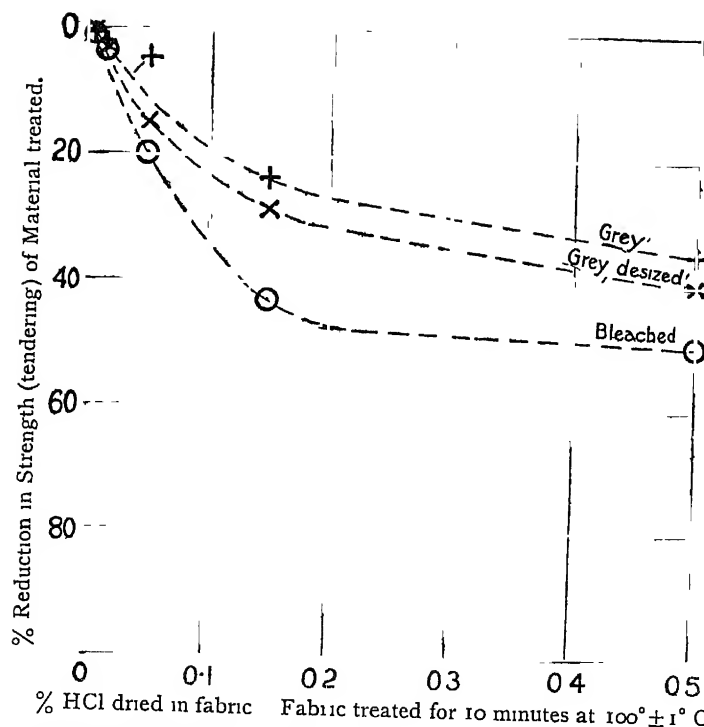
FIG. 42.—TENDERING OF COTTON FABRIC DRIED UP WITH HYDROCHLORIC ACID AT 100 %.
(Coward, Wood and Barratt)
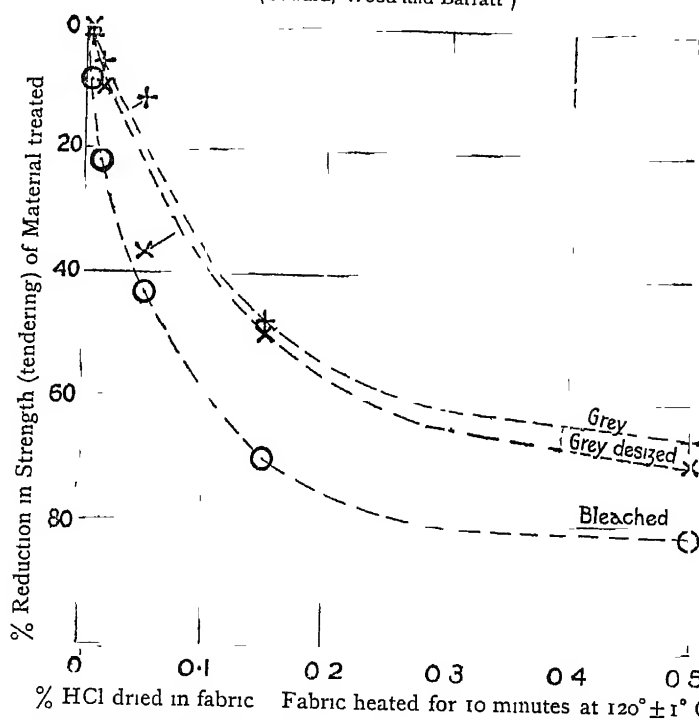
FIG 43 —TENDERING OF COTTON FABRIC DRIED UP WITH HYDROCHLORIC ACID AT 120° C
(Coward, Wood and Barratt)

boiled for $\frac{1}{2}$ hour in N/10 caustic soda, again well washed in water and dried, it was found to contain in one instance 1·14 per cent., and in another 0·97 per cent. of combined sulphur expressed as sulphuric acid The content of combined sulphur apparently gives the cotton an increased affinity for Methylene Blue, for when cotton is dried up with hydrochloric acid this property is less evident Thus, bleached cotton yarn was dried up at 50° C. with sulphuric acid of sp gr. 1·065, and hydrochloric acid of sp gr. 1·008, and the resulting copper numbers of the treated yarn being 5·2 and 5·1 respectively.   At the same time, a similar yarn was oxidised with acid and potassium permanganate (1/12 atom of oxygen per $C_6H_{10}O_5$) and found to have a copper number of 5·3   The three samples of yarn were then dyed with Methylene Blue and the dyestuff absorbed determined quantitatively by titration with titanous chloride   The following results were obtained :

TABLE LVIII

Sample	Content of Methylene Blue.
Bleached cotton	0 338 per cent
Sulphuric acid treated cotton	1 004 ,,
Oxidised cotton	0·747 ,,
Bleached cotton	0·345 ,,
Hydrochloric acid treated cotton . . .	0·282 ,,
Oxidised cotton	0·761 ,,

These results indicate that cotton tendered by drying-up with hydrochloric acid has a decreased affinity for Methylene Blue

It was further observed that although cotton tendered by drying-up with sulphuric acid somewhat resembles oxidised cotton in its increased for Methylene Blue and other basic dyes such as Rhodamine B and Crystal Violet and also by its decreased for direct dyestuffs such as Diamine Sky Blue, such acid-tendered cotton contains no oxidised cellulose.   Further, when acid-tendered cotton was boiled for $\frac{1}{2}$ hour with 5 per cent. caustic soda, its slight affinity for direct dyes persisted, whereas oxidised cotton after similar treatment regained its affinity for Diamine Sky Blue and other direct colours.

It is somewhat unfortunate that Knecht and Thompson have not recorded whether the cotton dried up with sulphuric acid retained an acid character after thorough washing with water.   A definite statement on this point would have helped one to have formed a theory as to how the sulphur was combined within the cotton.   Their results may, however, be compared with those of Coward,

Spencer and Wood (*Journ Text. Inst.*, 1923, xiv. 529) relating to the preferential absorption of sulphuric acid from solutions containing sulphuric acid In these investigations the preferential absorption of acid by cotton fabric was measured by determination of the change of hydrogen ion concentration by means of a hydrogen electrode. The results are shown in Fig 44, from which it is evident that the preferential absorption of sulphuric acid by cotton immersed in a bath of N/50 to N/1000 sulphuric acid is about 0·03 per cent. to 0·05 per cent.
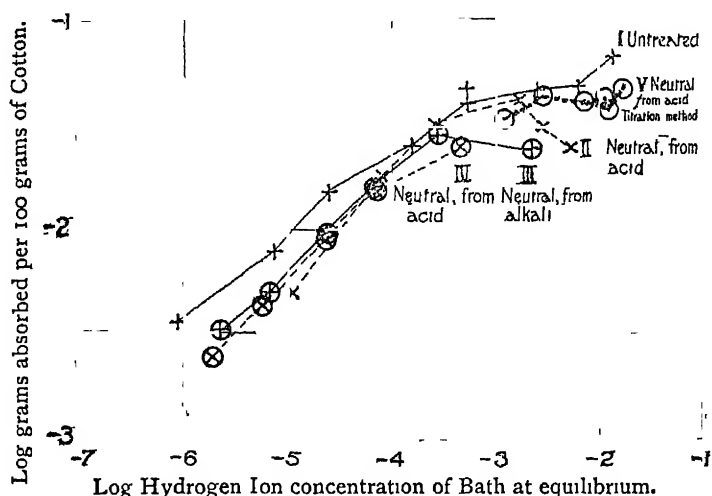
FIG 44 —PREFERENTIAL ABSORPTION OF SULPHURIC ACID BY
COTTON FROM DILUTE SOLUTIONS
(Coward, Wood and Spencer)

Curve 1 was obtained with untreated cotton fabric.
Curves 2 and 4 were obtained with pure commercial fabric which had been
      steeped in very dilute sulphuric acid and washed in tap-water till
      neutral to Methyl Red
Curve 3 was obtained with cotton fabric which had been treated with very
      dilute sodium hydroxide and well washed

These results indicate the difficulty found in technical practice in completely removing acids from cotton fabrics.

In view of the importance of small amounts of acid present in fabrics, the investigations of Coward and Wigley (*Journ Text Inst.*, 1922, xiii 121) are of interest. Two samples of bleached cotton fabric free from oxidised cellulose and size, one distinctly alkaline and the other distinctly acid, were repeatedly washed with pure water until they gave the same reaction when spotted with various indicators, with the exception of Methyl Red At that stage the fabric was shown to be neutral by treatment with 0·005 per cent. acid or alkali, and by means of such neutral fabric it was found possible to determine the accuracy with which

the acidity or alkalinity of a pure fabric could be shown by spotting with various indicators. The following table is based on the results obtained ·

TABLE LIX

Indicator	Acidity or Alkalinity of Fabric.	Colour of Spot
Thymol Blue . .	0·16 per cent H_2SO_4 and upwards	Purple
Methyl Orange. .	0 10–0·16 per cent. H_2SO_4	Intermediate (yellow-red).
Lacmoid . . .	0·06 per cent H_2SO_4 and upwards	Red
Lacmoid . . .	0 03–0·06 per cent H_2SO_4	Blue centre, red ring
KI+KIO$_3$+starch .	0·01 per cent and upwards.	Blue, increasing in intensity
Methyl Red . .	0 005 per cent H_2SO_4 and upwards	Red.
Methyl Red . .	0·005 per cent NaOH present as Na_2CO_3 and upwards	Yellow
Brom Thymol Blue.	0·02 per cent NaOH (present as Na_2CO_3)	Green.
Brom Thymol . .	0 04 per cent NaOH and upwards	Blue
Phenol Phthalein .	0·12 per cent NaOH and upwards	Pink, increasing in intensity.

A considerable amount of useful information has recently been obtained by Vincent (*Journ. Text. Inst*, 1924, xv. 281) relating to the change in tensile strength of cotton hairs and yarns produced by treatment with sulphuric acid In these investigations the cotton materials were steeped in acid solutions at room temperature for 48 hours, afterwards washed and slowly dried in air. The results obtained are shown in Table LX.

For single cotton hairs the curves obtained by plotting strength of acid against tensile strength, using the results shown in Table LX, are seen to be straight lines. Similar curves obtained for the yarns have definite breaks which are due to the fact that breakage of a yarn may be due to actual breakage or slipping of the cotton hairs of which it is made.

It was also found that kier boiling increases the tensile strength of cotton untreated yarn, but further weakens yarns which have been previously weakened by treatment with acid.

The data shown in Table LXI. were obtained by Farrow and Neale (*Journ Text. Inst*, 1924, xv. 157T), who determined the loss of strength of the single cotton hairs composing yarn which had been immersed for 2 days in cold sulphuric acid.

It is thus evident that when cotton is subjected to the action of cold sulphuric acid, it loses tensile strength in proportion to the concentration of the acid, and this proportion is almost a linear one.

TABLE LX

Sample Tested	Tensile Strength of Single Hairs in Yarn	Tensile Strength of Yarn
AMERICAN COTTON		
Untreated . .	5 38 g	4 57 ounces.
Treated with 10 per cent H_2SO_4 .	4 63	4 12 ,,
,, 20 ,, ,, .	4 04	3 87 ,,
,, 30 ,, ,, .	3 18	2·95 ,,
,, 40 ,, ,, .	2·54	2·25 ,,
,, 50 ,, ,, .	1 86	1 37 ,,
,, 60 ,, ,, .	1 23	0·72 ,,
,, 70 ,, ,, .	0 57	0 37 ,,
EGYPTIAN COTTON		
Untreated	5·35 g	0 60 ounces
Treated with 10 per cent H_2SO_4 .	5 00	8 96 ,,
,, 20 ,, ,, .	4 30	8·13 ,,
,, 30 ,, ,, .	3·01	6·75 ,,
,, 40 ,, ,, .	2 52	4 93 ,,
,, 50 ,, ,, .	1·60	3 27 ,,
,, 60 ,, ,, .	0 94	1 88 ,,
,, 70 ,, ,, .	..	0·93 ,,
,, 80 ,, ,, .	..	.

TABLE LXI

Grams of H_2SO_4 per 100 c c of Solution	Tensile Strength of Single Cotton Hairs
0	4 55 g
10	4 18
20	3 50
30	2 94
40	2 06
50	1·32
60	0 66
70	Nil

Saccharification by Means of Acids.

The saccharification of cellulose by means of acids, particularly sulphuric acid, is of considerable importance in the production of alcohol. It is probable that at some remote date, natural supplies of petroleum fuels will become exhausted or too expensive to work, and it would seem that alcohol is likely to be the best available substitute. For this reason numerous investigations are proceeding in which cellulose materials are hydrolysed by means of acids into sugar substances which may be further fermented into alcohol (see *Power Alcohol*, by Monier-Williams). In such processes, it is essential to obtain the maximum yield of sugars which are fermentable to alcohol, and when concentrated acids are employed for the hydrolysis, their subsequent neutralisation and even recovery are of considerable importance.

Budnikow and Solotarew (*Ber. Polyt Iwanowo-Wosniessensk*, 1921, iv. 119) record that when 1 g of filter paper is dissolved during 3 hours in 7–8 c.c. of 72 per cent. sulphuric acid and the resulting solution diluted so that it contains about 3 per cent. of acid and then heated for 2 hours at 120° C in an autoclave, a glucose solution containing not more than 0·6 per cent. of glucose is obtained. When this is fermented about 85 per cent. of the theoretical amount of alcohol is produced, and from 36–91 per cent. of the acid can be recovered by a somewhat costly electrolytic process.

Budnikow has later (*Zeit. angew Chem.*, 1923, xxxvi 326) reviewed various methods by which alcohol may be obtained from cellulose materials (sawdust, peat, etc.) by means of acids and also bacteria.

Klason has found that pinewood yielded 7·4 per cent. of fermentable sugars, calculated on the weight of dry wood.

It appears to be more difficult to obtain high yields of fermentable sugars by treating cellulose with dilute acids, since higher temperatures are necessary and destruction of the sugars formed occurs to a greater extent. Thus Ost and Wilkening (*Chem. Zeit.*, 1910, xxxiv. 461) obtained the following results by heating dextrose with dilute sulphuric acid at high temperatures ·

TABLE LXII

Initial Concentration of Dextrose	Strength of H_2SO_4	Duration of Heating	Temperature of Heating	Final Concentration of Dextrose
5 per cent	2 per cent.	3 hours	120° C	91·4 per cent
5 ,,	2 ,,	8 ,,	120°	70·3 ,,
5 ,,	2 ,,	1½ ,,	145°	67·7 ,,
5 ,,	2 ,,	5 ,,	145°	28 5–35·1 ,,

Budnikow and Sworykin (*Zeit. angew. Chem* , 1922, xxxv. 677) state that the disadvantage of using hydrochloric acid for the technical hydrolysis of cellulosic materials for the production of alcohol and sugars, lies in the difficulty experienced in removing excess of acid from the resulting sugar solutions.   By electrolytic methods, however, these workers claim to be able to remove 98·7 per cent. of the acid without loss of sugar.   Using such a method, peat was saccharified with hydrochloric acid to the extent of 33–34 per cent

CHAPTER V

COTTON AND VARIOUS REAGENTS

ALTHOUGH cotton is generally assumed to be very inert, yet it is affected by many agents and influences, such as light, oxygen, bacteria, mechanical treatment and even solutions of neutral salts. Usually, however, the conditions necessary for the rapid attack of cellulose by these means do not obtain under the circumstances in which this substance is employed

Thus in their investigations of the mercerisation of cotton with caustic soda, Pope and Huebner (*Journ Soc. Chem Ind*, 1903, xxii 70) found that when a saturated solution of potassium iodide was poured on cotton, it was quickly wetted-out and became glassy and transparent. Shrinkage of the cotton hairs also occurred. It was found that the cotton retained 15 per cent of KI after being washed with absolute alcohol ; and though the product soon became brown when exposed to light, this did not occur *in vacuo* All the potassium iodide could be removed with water, but the resulting yarn had a greater tensile strength and a greater affinity for direct dyes such as Benzopurpurine 4B

It was similarly found that saturated solutions of barium iodide and potassium mercuric iodide had a similar effect on cotton Treatment of mercerised cotton yarn with a saturated solution containing potassium iodide produced a diminution of tensile strength.

Various other solutions of neutral salts have been found to attack cotton, and in some instances dissolve it. Recently, Williams (*Manchester Memoirs*, 1921, lxv. 12, and *Journ Soc Chem. Ind*, 1921, xl. 221) has recorded his observations on the action of cotton of various solutions containing thiocyanates, double thiocyanates, calcium chloride magnesium and zinc chlorides. Most of these solutions, when of a viscous nature, are able to dissolve cellulose, and Williams has shown that this solvent property is largely dependent on the boiling-point, the viscosity and the heat of dilution.

Cellulose Xanthate.

The solvent power of a mixture of carbon disulphide and caustic soda on cotton has had remarkably important technical results, since by means of such solutions the most important type of artificial silk is now being manufactured. This reaction of cellulose was discovered by Cross Bevan and Beadle in 1891, when these workers found that if cotton was steeped in 17–18 per cent caustic soda, pressed so that the product had the composition

Cellulose	. .	25 per cent.
Caustic soda .	.	13 ,,
Water	. .	62 ,,

and then stirred with carbon disulphide, it gradually dissolved to form a very

viscous solution which was comparatively stable Such a solution is termed viscose and is prepared substantially in the same manner to-day for the manufacture of artificial silk

For the preparation of viscose, the constituents are brought together in approximately the proportions

$$C_6H_{10}O_5 \quad 2NaOH \quad CS_2$$
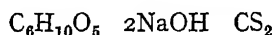
and the soluble cellulose xanthate thereby formed has the structure

$$C{=}S\begin{array}{l} \diagup O{-}C_6H_9O_4 \\ \diagdown SNa \end{array}$$
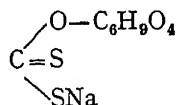
and is therefore expressed as a sodium salt of xanthogenic acid

$$C{=}S\begin{array}{l} \diagup O\ X \\ \diagdown SH \end{array} \qquad X = \text{any radical.}$$
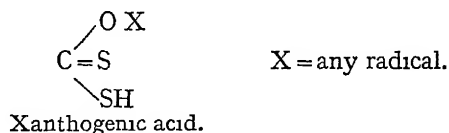
Xanthogenic acid.

Other salts of xanthogenic acid are known and may be prepared by method of double decomposition Thus when a solution of a heavy metal such as aluminium, copper, zinc or lead is added to sodium cellulose xanthate the insoluble metallic cellulose xanthate is precipitated Ammonium cellulose xanthate is not so stable as the sodium salt and rapidly decomposes with regeneration of cellulose.

When a solution of sodium cellulose xanthate is allowed to stand out of contact with air, it slowly changes and ultimately becomes cloudy owing to precipitation of cellulose Cross and Bevan consider this change to be due to gradual elimination of carbon disulphide residues, so that the solution contains a xanthate whose cellulose content simultaneously increases. The progress of this change may be followed by titration with iodine, when the following reaction takes place ·

$$2\,C{=}S\begin{array}{l}\diagup O\ C_6H_9O_4\\\diagdown SNa\end{array} + I_2 \longrightarrow 2\ NaI + \left(CS\begin{array}{l}\diagup O\ C_6H_9O_4\quad O_4H_9C_6\ O\diagdown\\\diagdown S{-}S\diagup\end{array}S{=}C\right)$$
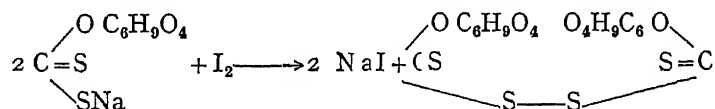
Stages in this decomposition may be detected During the first day the following change occurs

$$C{=}S\begin{array}{l}\diagup O\ C_6H_9O_4\\\diagdown SNa\end{array} \longrightarrow C{=}S\begin{array}{l}\diagup O\ C_{12}H_{19}O_9\\\diagdown SNa\end{array}$$
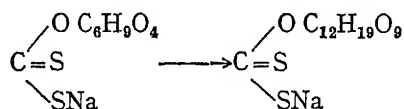
and during the next 7 days the following change ·

$$\begin{array}{cc} C{=}S \underset{\diagdown \text{SNa}}{\overset{\diagup \text{O.C}_{12}\text{H}_{19}\text{O}_9}{}} & {>}C{=}S \underset{\diagdown \text{SNa}}{\overset{\diagup \text{O C}_{24}\text{H}_{39}\text{O}_{19}}{}} \end{array}$$
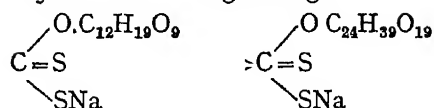
Afterwards the separated product contains practically no sulphur or sodium and consists of regenerated cellulose, having the same composition as cotton— $C_6H_{10}O_5$.

Although the regenerated cellulose has the same composition as purified cotton, it has not the same physical properties   Thus, under ordinary conditions, it retains more moisture, and generally it has a greater activity towards dyestuffs.

Working under careful conditions, the following cycle can be established

$$\begin{array}{c} \text{NaOH} \\ \text{Cellulose} \quad \xrightarrow{\quad} \text{Cellulose xanthate} \\ \text{100 parts} \quad \text{CS}_2 \qquad \text{130 parts} \\ \diagup \\ \text{Cellulose.} \\ \text{103 parts} \end{array}$$
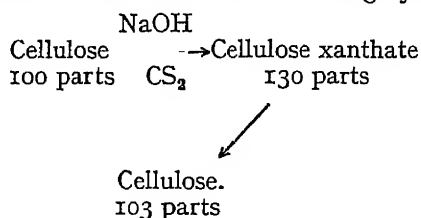
In some instances the degree of purity of a cellulosic material can be determined by carrying out the above cycle.

The properties of viscose solutions have been chiefly investigated from a technical standpoint, and these are referred to in Chapter IX.

Effect of Mechanical Stress on Cotton.

Apart from the action of acids, alkalis or other reagents, cotton appears to be capable of degradation by purely mechanical processes.   Fort appears to have first noticed this phenomenon (*Journ. Soc Dyers & Col.*, 1918, xxxiv 215), having observed the powdering of some cotton during operations of beetling. Some of the product was forwarded to Cross and Bevan (*Journ Soc. Dyers & Col*, 1918, xxxiv. 215), who found it to consist of small particles which were inert towards polarised light, thereby differing from cotton which shows marked changes of colour.   The powdered cotton was also shown to be soluble in 17·5 per cent. caustic soda to the extent of 40–56 per cent. and from the alkaline solution a large proportion of cellulose could be precipitated by addition of acids   This cotton therefore contained a much larger proportion of β- and a-cellulose than when in its original state

Subsequently Warr (*Journ. Soc Dyers & Col*, 1923, xxxix. 361) drew attention to the presence of powdered cotton, resembling grains of sago, in a cotton rope used on a main drive.   That this product was the result of combined friction and pressure appeared likely, and Warr therefore sought to imitate it by drawing a smooth glass rod across a piece of wet calico stretched upon a sheet of glass. He found that when the calico was afterwards dyed with a vat, sulphur or direct

dye, the path of the rod could be clearly seen, though less prominently when dyed with basic or mordant colours.

More recently, Fort (*Journ Soc Dyers & Col*, 1924, xl. 142) has discovered the conditions under which cotton can be mechanically powdered as desired (previous efforts to reproduce the product formerly obtained were unsuccessful). Fort now considers that powdered cotton is the product of abrasion of cellulose fibres grinding on each other under limitations imposed by the following conditions

1 An unusually close approach to the maximum of close contact between fibres
2 A repeated movement, such as bending, shearing or twisting of layers of compact fibres
3 External compression must be maintained constantly to avoid displacement and escape of the fibres suffering abrasion on each other

Powdering of cotton fabric during beetling may first show itself in the form of " chalky " patches which consist of splintered fibres to which the powdered cotton adheres. When this powder is treated with hydrochloric acid the grains open and reveal themselves as " balled-up " shreds of splintered fibres. Fort observes that once the formation of powder has occurred, further formation is accelerated by the abrasive nature of the powder initially formed, and this agrees with the further observation that powdering is encouraged by extraction of the natural fats and waxes from the cellulosic material.

Now that the production of powdered cotton can be controlled, it is likely that this type of degrading action will be further examined

Action of Heat on Cotton.

When cotton is heated at temperatures above 150° C. or at lower temperatures for prolonged periods, it suffers complete decomposition and the products are very complex Knecht (*Journ. Soc. Dyers & Col*, 1920, xxxvi 195) has shown that when cotton is heated at about 80° C. for 336 hours, it gains distinct reducing properties

At temperatures above 250° C , Cross and Bevan have indicated that cotton forms the following products ·

TABLE LXIII

Solid 30 per cent	Liquid : 50 per cent	Gaseous : 20 per cent
Charcoal.	Containing . Acetic acid, methyl alcohol, acetone, furfural, tar	Chiefly CO and CO_2

A considerable amount of work has been carried out in the dry distillation of cellulose obtained from wood   Klason (*Zeit angew Chem*, 1909, xxii 1205 ; 1920, xxiii 1252) has recorded the following products

TABLE LXIV

Product	Quantity
Water	34 52 per cent.
Acetic acid . . .	1 39 ,,
Acetone . .	0 07 ,,
Tar . . .	4 18 ,,
Charcoal	38 82 ,,
Other organic compounds .	5 14 ,,
Gases $\begin{cases} CO_2 \\ C_2H_4 \\ CO \\ CH_4 \end{cases}$ . . .	10 35 ,,
	0 17 ,,
	4 15 ,,
	0 27 ,,

Other substances observed among the products of dry distillation of cotton are furfural, phenol, cresol, methylethyl ketone, furane, methylfurane, 2 5-di-methylfurane, tri- and tetra-methylfurane, toluene, hydroxymethylfurfural, γ-valerolactone, but further work is required before these observations can be interpreted correctly from the standpoint of the structure of cellulose

Cotton and Solutions of Sodium Chloride.

An interesting observation of Harrison (*Journ Soc Dyers & Col*, 1912, xxviii 359) showed that when a solution of sodium chloride was filtered through cotton the filtrate was acid   Subsequently in connection with some tissue paper used for wrapping lenses, it was observed that some of the papers gave a slightly acid liquor on extraction with a solution of neutral sodium chloride, and this was further investigated by Masters (*Journ Chem Soc*, 1923, cxxiii 2026)

Masters used purified cotton wool (the previous treatment of this is not stated), and found that when this was extracted with cold N/10 NaCl solution the filtrate was definitely acid   Repeated extraction did not appear to diminish the quantity of acid found in the filtrate   Further, when the extracted cotton was afterwards treated with pure water, the filtrate was found to be slightly alkaline. On the whole, the total amount of acid extracted by treatment with solutions of sodium chloride was approximately equal to the total amount of alkali extracted by alternate extractions with pure water   It would therefore appear that cotton has the power to decompose sodium chloride.

Chemically Treated Cotton and Solvent Extraction.

In a previous chapter some account has been given of the fatty matters present in raw cotton and their complex nature indicated. It has also been discovered that the extraction of these substances by means of organic solvents is not so simple as at first appears

Knecht (*Journ Soc Dyers & Col*, 1920, xxxvi 196) noticed that bleached cotton yarn (therefore presumably free from waxes and fats) after being heated for 336 hours in a sealed tube at 93° C yielded the following extract ·

<div align="center">

Benzene extract . . 0·3 per cent
Alcohol ,, . . 0 6 ,,

</div>

and it therefore appeared probable that the operations of bleaching and heating were capable of rendering otherwise inaccessible fatty matters within the cotton accessible to solvent extraction

In confirmation of this, Knecht exhaustively extracted some grey Egyptian cotton yarn with benzene, bleached it, and again obtained a further quantity of fatty matter on extraction with benzene Mechanical treatment of cotton also increased its extractive matters

Knecht and Streat (*Journ Soc Dyers & Col*, 1923, xxxix 73) have continued these investigations In a first series of experiments raw cotton was extracted with benzene to yield extract A

The dry extracted cotton was then steeped in 2° Tw hydrochloric acid at 30°–40° C for 15 minutes, washed, dried and again extracted with benzene, yielding extract B

Subsequently, the cotton was boiled for 15 minutes in 5° Tw hydrochloric acid, dried without washing, ground to powder, sieved through calico and extracted with benzene to yield extract C

The following results were obtained

<div align="center">

TABLE LXV

</div>

Type of Cotton	Extract A	Extract B	Extract C	Total Extract.
American . .	0·63 per cent	0 21 per cent	0 39 per cent	1·22 per cent
Egyptian . .	0 56 ,,	0·14 ,,	0·23 ,,	0·92 ,,
Indian .	0·45 ,,	0·17 ,,	0·28 ,,	0 89 ,,
Queensland .	0 46 ,,	0 28 ,,	0·30 ,,	1·04 ,,
Nigerian .	0 57 ,,	0 21 ,,	0·18 ,,	0 96 ,,

All these extracts were brown waxy solids, B and C being lighter in colour than A.

In a second series, raw cotton was boiled in 5° Tw. hydrochloric acid for 15 minutes, dried without washing, ground and sieved through calico and then extracted with benzene, thereby yielding the following extracts :

TABLE LXVI

Type of Cotton	Extract.
American . . .	0·74 per cent.
Egyptian	0 64 ,,
Indian	0 67 ,,
Queensland . . .	0 60 ,,
Nigerian	0 72 ,,

In the third series, raw cotton was ground between steel rollers revolving at different speeds, sieved through calico and extracted with benzene thus :

Type of Cotton	Extract.
American . .	1·20 per cent.
Egyptian . .	1·00 ,,

The relative effects on the extractive matter may be seen in the following table :

TABLE LXVII

Type of Cotton.	Extract · Series 1.	Extract Series 2	Extract Series 3.
American . .	1·22 per cent.	1·20 per cent	0·74 per cent
Egyptian . .	0·92 ,,	1 00 ,,	0·64 ,,

It is thus evident that the yield of extractive matter from mechanically powdered cotton is nearly equal to the sum of the three extracts after three chemical treatments, and that chemically disintegrated cotton yields a much sm ller extract.

Although this appears to indicate that the fatty matters in raw cotton differ in accessibility, Clifford, Higginbotham and Fargher do not agree with this and refer to the differing solubilities of the numerous substances shown to be present in cotton

Less unexpected is the fact that the quantity and probable nature of extractive matter obtained from cotton is dependent on the solvent used, and in commercial practice this is of importance   Fort (*Journ. Soc. Dyers & Col*, 1923, xxxix 44) finds that the higher boiling solvents extract the greater amount of fatty matters.   Thus the following results were obtained with a particular linen (the corresponding figures for cotton are unfortunately not given)

TABLE LXVIII

Solvent.	Extract.
Benzene (b p 80° C) .	1·65 per cent.
Toluene (b p 112° C.)	1·83 ,,
Xylene (b p 137°–142° C.) .	1·87 ,,
Carbon tetrachloride (b p. 77° C)	1·57 per cent.
Tetrachlorethane (b p. 147° C) .	1·90 ,,

Fort claims a substantial advantage of high boiling solvents over ordinary low boiling solvents such as ether, petroleum ether, chloroform, carbon bisulphide and acetone, both because of their greater extractive power and their adaptability in the treatment of wet fabrics.

Methods of Solvent Extraction.

The use of solvents in the extraction of cotton may, however, be varied almost indefinitely, since time, temperature and nature of solvent play such important parts

Successive extraction with various solvents also opens up further possibilities   Thus Knecht and Streat (*supra*) obtained the following results by extracting 10 g. of raw cotton in a 200 c c. capacity Soxhlet extractor

9

(the solvent was allowed to syphon over ten times) using benzene and then alcohol .

TABLE LXIX

Type of Cotton.	Extract with Alcohol.	Extract with Benzene	Total.
American . .	0·65 per cent	0·18 per cent.	0·83 per cent.
Egyptian . .	0·875 ,,	0·155 ,,	1·03 ,,
Indian . . .	1·31 ,,	0·20 ,,	1·51 ,,
Queensland . .	1·83 ,,	0·29 ,,	2·12 ,,
Nigerian . .	1·10 ,,	0·35 ,,	1·45 ,,

Clifford, Higginbotham and Fargher give the following summary extraction of data obtained with American and Egyptian cottons   The extractions were carried out on 100 g of the raw cotton using 1200 c.c. of solvent.

TABLE LXX

Solvent.		American Cotton. Per cent Extract after				Egyptian Cotton. Per cent Extract after			
		1 hr.	4 hrs.	16 hrs	32 hrs.	1 hr.	4 hrs	16 hrs	32 hrs
Light petroleum (b p. 40°–60° C.)	Cold	0·28	0·38	0·44	0·46	0·15	0·26	0·34	0·38
	Hot	0·25	0·42	0·50	0 52	0·21	0·28	0·35	0·37
Light petroleum (b p. 60°–70° C)	Cold	0·34	0·44	0·47	0·48	0·27	0·35	0·40	0·43
	Hot	0·42	0·48	0·50	0·52	0·35	0 37	0·41	0·43
Ether . . .	Cold	0 41	0·48	0 52	0·54	0·26	0·40	0·47	0·51
	Hot	0·45	0 55	0·58	0·59	0·33	0·43	0·51	0·56
Benzene . .	Cold	0·45	0·54	0·57	0 58	0·34	0 43	0·50	0·54
	Hot	0·46	0·56	0·59	0·60	0·46	0·54	0·63	0·67
Carbon tetrachloride	Cold	0·40	0·51	0·57	0·59	0·33	0·42	0·46	0·49
Chloroform . .	Cold	0·52	0·60	0·62	0·63	0·49	0·57	0·62	0·65
	Hot	0·67	0 76	0·78	..	0·52	0 61	0 68	0·72

Some interesting results were obtained by the same workers by successively extracting American cotton with four different solvents, the order being varied.

TABLE LXXI

Successive Extraction with			Extract	Successive Extraction with			Extract.
Chloroform	.	.	0·622 per cent	Light petroleum	.	.	0·421 per cent.
Benzene	.	.	0·018 ,,	Ether	.	.	0·076 ,,
Light petroleum	.	.	0·004 ,,	Benzene	.	.	0·109 ,,
Ether	.	.	0·010 ,,	Chloroform	.	.	0·048 ,,
Total	.	.	0·654 per cent	Total	.	.	0 654 per cent.
Ether	.	.	0·487 per cent	Benzene	.	.	0·554 per cent.
Light petroleum	.	.	0·009 ,,	Ether	.	.	0·053 ,,
Chloroform	.	.	0·138 ,,	Light petroleum	.	.	0 004 ,,
Benzene	.	.	0·020 ,,	Chloroform (by difference)			0·043 ,,
Total	.	.	0·654 per cent.	Total	.	.	0·654 per cent.

Successive extraction of Egyptian cotton with various solvents yielded the following results :

TABLE LXXII

Solvent			Extract (8 hours).
Chloroform	.	.	0·550 per cent
Benzene	.	.	0·043 ,,
Ether	.	.	0 033 ,,
Petrol	.	.	0·007 ,,
Total	.	.	0 633 per cent

Extraction of the same cotton with chloroform for 32 hours yielded an extract of 0·655 per cent.

Methods for characterising the fatty extracts obtained by solvent extraction

are described in Chapter X., but the following details were obtained for the 8-hour extracts of Egyptian cotton

TABLE LXXIII

Solvent.		M Pt	Acid Value	Saponification Value.	Ester Value	Unsaponifiable Value
Petrol (b p. 40°–60° C.)	.. ..	73° C 74°	25 24	57 46	32 22	62 68
Petrol (b.p. 60°–70° C.)	.	73·5° 78°	24 32	65 73	41 41	49 64
Ether . . .	Cold Hot	72·5° 75°	30 36	77 90	47 54	55 53
Benzene . .	Cold Hot	78° 81°	29 32	77 77	48 45	48 38
Chloroform . .	Cold Hot	112° 114°	33 35	79 85	46 50	43 34
Carbon tetrachloride Cold		80°	33	82	49	45

In the above, the striking difference in the m p of the chloroform (both hot and cold) extract and that of other extracts is apparent. The extracts also appear to be largely influenced by the temperature of their extraction. These results, taken with those which follow and which were obtained on the extracts from long period extracts of American cotton, support the experimental observation that benzene and chloroform tend to dissolve material of a resinous character more readily in the case of Egyptian cotton than in that of American cotton

For purposes of comparison, some properties of extracts obtained from sized cotton fabrics are given on opposite page. These were determined (also all given on opposite page) by Clifford, Higginbotham and Fargher

Solvent extraction, as previously indicated (page 44) is of limited importance in the bleaching of cotton and linen since it enables the complete removal of fatty matters to be carried out Unsaponifiable mineral oils and waxes are the source of much trouble in dyeing and finishing, since they are not removed by the processes of kiering and bleaching as ordinarily performed.

Cotton Strength and Solvent Extraction.

Lloyd (*Journ. Soc Dyers & Col.*, 1921, xxxvii 165) states that in one instance the bleaching of cotton warps resulted in a loss of strength of 15–20 per cent. ;

TABLE LXXIV

Extract

Solvent.		M Pt	Acid Value	Saponification Value	Iodine Value (Hanus)	Acetyl Value	Unsaponifiable Value	Acetyl Value of Unsaponifiable Matter
Light petroleum (40°–60°C)	Cold	73 5° C	31	88	31	45	56	118
	Hot	73 5°	19	58			60	.
Light petroleum (60°–70° C)	Cold	74°	26	56		.	66	
	Hot	74°	16 5	58			59	
Ether	Cold	77°	24	91	32	67	69	130
	Hot	78 5°	27	67	.		50	
Benzene	Cold	75 5°	29	65	30	73	52 5	128
	Hot	81·5°	29	65			61	
Chloroform	Cold	76°	30	96	32	61	60	112
	Hot	81°	119	161			42 5	114
Carbon tetrachloride	Cold	75°	30	66			56	

TABLE LXXV

Softener in Size	Solvent	Amount of Extract in in 6 hours	Acid Value	Saponification Value	Unsaponifiable Value	Iodine Value.
Tallow	Petrol (hot)	0 81 per cent	22	141	28	.
,,	Carbon tetrachloride (cold)	0 88 ,,	20	158	24	.
,,	Chloroform (hot)	0 98 ,,	25	143	26	
,,	,,	0 93 ,,	18	143	24	.
Unknown	Carbon tetrachloride (hot)	0 66 ,,	35	136	31	.
,,	,, ,,	1 00 ,,	28	129	36	
,,	,, ,,	0 60 ,,	25	127	46	
,,	,, ,,	0 88 ,,	30	126	33	.
Castor oil	Chloroform (hot)	2 29 ,,	28	173	15	49

when those warps were solvent extracted, the subsequent bleaching could be effected in a less drastic manner and the loss of strength reduced to less than 10 per cent.

The removal of fatty substances from cotton must also affect its elasticity, plasticity and strength. As regards the latter property, Knecht and Fernandes (*Journ. Soc. Dyers & Col.*, 1920, xxxvi 46) have compared the strength of

American and Egyptian cotton yarns before and after extraction with benzene, alcohol and water, their results being as follows ·

<div align="center">

TABLE LXXVI

AMERICAN COTTON

</div>

	Original	Conditioned.	Dried at 100° C.
Original.		12·19 oz	13·32 oz.
Benzene extracted		15·19 ,,	14·52 ,,
Alcohol ,, ...		14·59 ,,	14·37 ,,
Water ,, ...		16·12 ,,	15·92 ,,

<div align="center">

EGYPTIAN COTTON

</div>

	Original	Conditioned.	Dried at 100° C.
Original		15·34 oz.	15·51 oz
Benzene extracted		18·02 ,,	16·01 ,,
Alcohol ,, ...		17·10 ,,	16 81 ,,
Water ,, ...		15·45 ,,	15·59 ,,

It is noticeable that for both American and Egyptian cottons, the strength is increased by drying at 100° C. whereas after solvent extraction it is decreased by this treatment   This is related to the fact that bleached cotton shows a decrease of strength when dried at 100° C.

Cotton and Light.

The well-known fact that curtains lose considerable strength when exposed to the sun is evidence of the degrading action of light on cellulose   As yet, however, this action has been but little investigated.

Observers generally agree that the visible portion of the spectrum has much less effect than the ultra-violet rays.   Thus Witz (*Bull Soc Rouen*, 1883, xi 188) found that blue light produced oxycellulose (see Chapter VI.) while red and yellow light had no action, and Scheurer (*Bull Soc Ind. Mulhouse*, 1910, lxxx. 324) found that light of 3000°–1860° A was that responsible for oxidation.

At one time, the outer envelopes of airships were impregnated with yellow lead chromate in order to cut off harmful light of short wave-length.   During the war, the necessity for protecting aeroplane fabrics from weathering was an incentive to research work relating to the action of light on cotton and linen.   Turner (*Journ Soc. Dyers & Col.*, 1920, xxxvi 165) states that light was finally found to be the most potent agency in the weathering of fabric, and cellulose dopes con-

taining pigments for cutting off the light were subsequently largely used with success.

By means of a quartz mercury arc, Aston showed that light of wave-length greater than 3660° A. has no destructive effect on linen, but that the nature of the gas surrounding the linen material has a considerable influence. For instance, Aston obtained the following results by exposing linen threads to light from a mercury arc

TABLE LXXVII

Atmosphere surrounding Linen.	Loss of Strength.
Air (not dried) . . .	34 per cent
,, (dried)	34 ,,
Vacuum	10 ,,

Replacement of air by hydrogen also led to a decreased loss of strength.

Vignon has found that linen which suffered a loss of strength of 20 per cent. when exposed to light in a dry atmosphere, decreased in strength by 31 per cent. when the atmosphere was humid. On the other hand, Barr found an increased loss of strength in dry air. The effect of moisture is therefore not accurately known.

Harrison (*Journ Soc. Dyers & Col*, 1912, xxviii. 225) found that cotton, when exposed to the light from a mercury arc, acts as a reducing agent and is able to reduce Flavanthrene and itself form oxycellulose. After such exposure, cotton has an acidic reaction, partly dissolves in water and is able to reduce Fehling solution and ammoniacal silver nitrate.

The action of ultra-violet light from a Hewitt-Cooper lamp on cotton has also been investigated by Doree and Dyer (*Journ Soc Dyers & Col*, 1917, xxxiii. 17) Aeroplane fabric was stretched across a wood frame and exposed for one week at 30°–35° C., during which time the exposed surface became biscuit-coloured. Tests on the fabric before and after exposure yielded the following results :

TABLE LXXVIII

Test	Before Exposure.	After Exposure
Loss in weight in boiling 1 per cent NaOH, 5 minutes	0·0 per cent	9·5 per cent
Loss in weight in boiling 1 per cent NaOH, 60 minutes .	1·0 ,,	13·6 ,,
Copper number . . .	0 62 ,,	4·0 ,,
Furfuraldehyde produced by distillation with HCl . .	0·20 ,,	1·34 ,,
Absorption of Methylene Blue .	0·70 ,,	1·50 ,,
Strength of yarn in grams .	110 ,,	Nil.

The action of the light was therefore such as to destroy completely the tensile strength of the fabric and increase its reactivity and solubility. Further, the exposed fabric partly dissolved with a golden yellow colour in cold 10 per cent. caustic soda, a behaviour characteristic of oxycellulose (see Chapter VI.).

It was also found that rays from radium rapidly destroyed cotton

Light therefore appears to have an oxidising action on cotton and linen, producing results similar to the action of ozone (see page 150), and it is perhaps for this reason that it has been assumed that the destructive action of light is due to formation of ozone This assumption, however, rests on slender evidence

An early observation by Hartley (*Journ Chem Soc* , 1893, lxiii 243) that the whole of the ultra-violet end of the spectrum as far as 2000λ is rendered visible when allowed to fall on a sheet of white blotting-paper, has since been investigated by S. Judd Lewis (*Journ Soc. Dyers & Col*, 1918, xxxiv. 167 , 1921, xxxvii. 201 ; 1922, xxxviii. 68, 99 ; 1924, xl 29, 111). This fluorescence is without colour, and so distinct are the lines of cadmium made visible, that they may be well focused on such a screen.

In the first part of his investigations, Lewis allowed an ultra-violet spectrum to fall on fibrous material in sheet form, and the luminous glow produced thereon was then observed from the side of the sheet distant from the source of light. The glow was therefore observed by transmission, and its intensity could be easily estimated qualitatively.   Thus, accepting some WT Bank paper (15 lb. per ream) as a standard, Lewis found

TABLE LXXIX

Material	Intensity of Fluorescent Glow.
Filter paper	Better than standard
Figured viscose artificial silk .	Perhaps the best
Fabric, cotton warp and viscose weft .	Very good
Normal and acetylated cotton fabrics .	Very good and but little difference between them
Paper treated with ethyl malonate .	Not at all good
Normal paper	Decidedly good
Ligno-cellulose paper . . .	Not good
Acetylated paper. . .	Very strong
Nitrocellulose paper, 60 per cent . .	Very little fluorescence
,, ,, 50 ,, . .	Little or no fluorescence
,, ,, 40 ,, . .	No fluorescence

The luminous glow transmitted through the sheet material was found to be affected by the thickness of the sheet, so that for quantitative work it was

subsequently found better to use a method of "reflection." The apparatus designed for this is shown in Fig. 45.

L is a rotating (cooled) tungsten arc which is focused by means of the sphero-cylindrical condenser C on to the slit S of a Hilger quartz spectro-graph. A full spectrum falls on the glass plate AB, on which is mounted the paper or fabric under examination. That part of the spectrum comprising ultra-violet light of 2100–3300λ falls on AD, where it is partly reflected and to a much larger extent degraded by the cellulosic material to visible light which is emitted from the surface of the material in all directions. Both reflected ultra-violet light and emitted visible light are collected by the lens G of a photographic apparatus M placed perpendicularly to AD , but since the lens G is of glass, the reflected ultra-violet is all filtered out   The photographs (see Fig. 46) therefore record the intensity of the emitted or fluorescent light from AD.

The use of this apparatus for the quantitative measurement and comparison
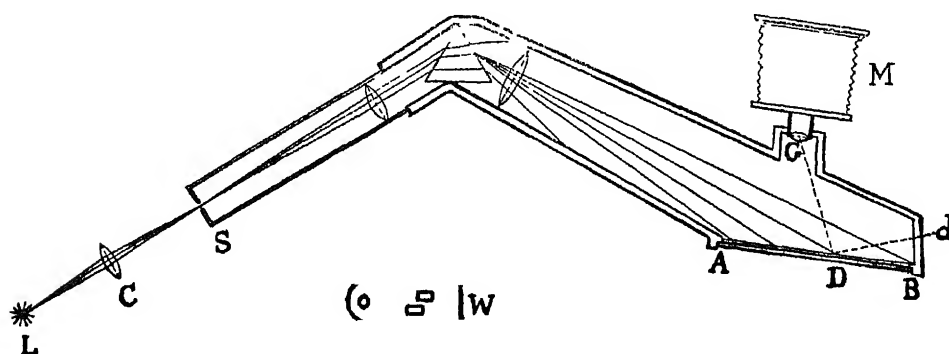

FIG. 45.—APPARATUS FOR MEASURING THE FLUORESCENT POWER OF CELLULOSE.
(Lewis)

of fluorescent power rests on the assumption that the intensity of the fluorescent effect is proportional to the time of exposure, an assumption which is most probably true.   Thus, the standard (now a special pure paper) and another specimen of cellulose are exposed to the ultra-violet part of the spectrum, and a photograph taken during an exposure of, say, 100 minutes   Subsequently, other photographs are taken, the exposures being, for the standard, say, 90, 80, 70, 60, 50, 40, 30, 20 and 10 minutes

Comparison of the photographs (see Fig. 46) will then indicate that at some particular wave-length the intensity of the fluorescence of the specimen is exactly equal to that of the standard at the same wave-length, but produced by an exposure of, say, 90 minutes.   Thus the specimen has required 100 minutes to produce the same effect on the photographic plate as that produced by the standard in 90 minutes   The fluorescent power of the specimen will in this case be considered as 90 per cent. of that of the standard.
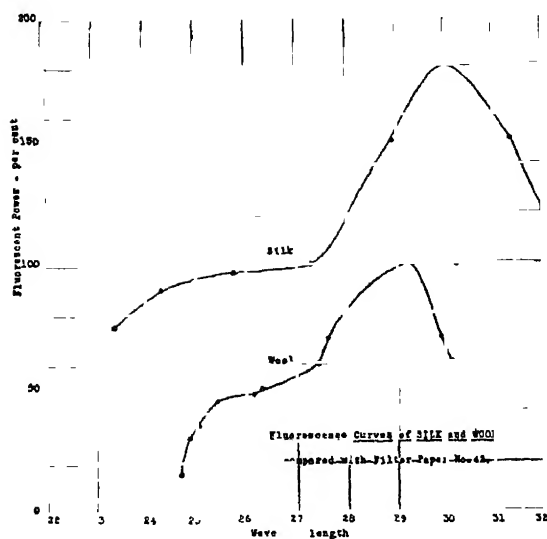
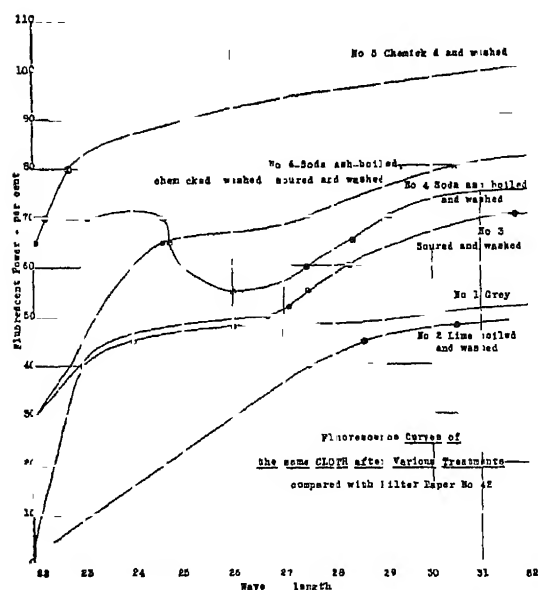FIG. 47.—FLUORESCENT CURVES OF SILK AND WOOL

(Lewis.)

FIG. 48.—FLUORESCENT CURVES OF TREATED COTTON.

(Lewis.)

In this manner, the fluorescent power of the specimen may be determined in relation to the standard at various wave-lengths, that is, in every region of the spectrum. The results are expressed in the form of curves, the fluorescent powers being represented by ordinates and the wave-lengths by abscissæ. Lewis finds the shape of these curves to have considerable significance.

Although these investigations have been concerned mainly with cotton and cellulose materials, it was shown that silk and wool (see Fig. 47) have characteristic fluorescent powers. For the effect of industrial treatment see Fig 48, in which the fluorescent properties of the same piece of cotton fabric are shown when (1) grey, (2) lime boiled and washed, (3) soured and washed, (4) soda ash boiled and washed, (5) chemicked and washed, (6) soda ash boiled, chemicked, washed, soured and washed

At present, the evidence is insufficient to justify a conclusive statement, but it is extremely likely that the fluorescent power of a cellulosic substance is not related to its physical condition. For instance, cellulose acetate in the forms of paper, powder and transparent films yield fluorescent curves of close similarity, and similar curves are also obtained for hydrocellulose prepared by different methods It is therefore probable that the shape of a curve is dependent on the chemical structure of the substance.
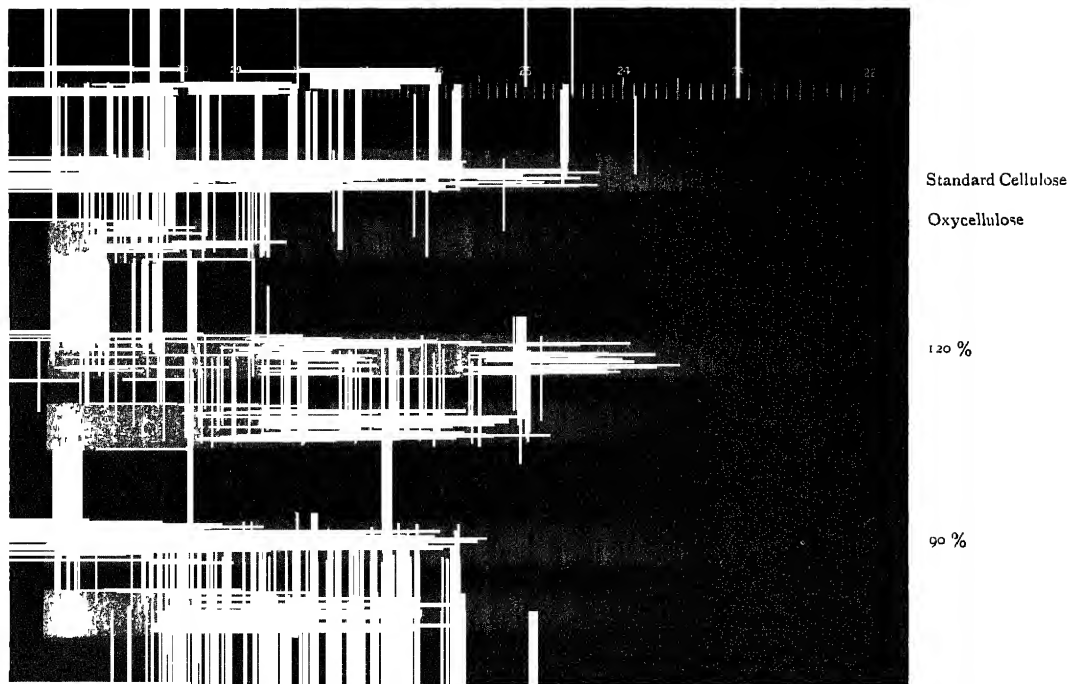
FIG 46—PHOTOGRAPHS OF CELLULOSE AND OXYCELLULOSE FLUORESCENCE.

(Lewis)

Lewis has distinguished six types of curves, *a, b, c, d, e* (see Fig. 49), which are representative of the following substances :

  a. Pure papers (from cotton).
  b. Pure cellulose—cotton wool, purified cellulose from wood, linen, regener-

ated cellulose from viscose and solutions of cotton in sulpho-cyanides   See Fig 50

c Hydrocellulose, prepared from cotton by the treatment with various acids. See Fig. 51.

d. Oxycellulose — prepared from cotton by oxidation or exposure to ultra-violet light. See Fig 53.

e. Cellulose acetate   See Fig 52.

f. Acid derivatives of cotton, *e g.* parchmentised cotton.

These investigations have brought to light a number of very interesting and valuable facts concerning cotton, but it is evident that more facts are required before the results obtained can be correlated to a theory   It seems likely, however, that methods are being discovered which may enable those in charge of textile processes to follow these conveniently and scientifically
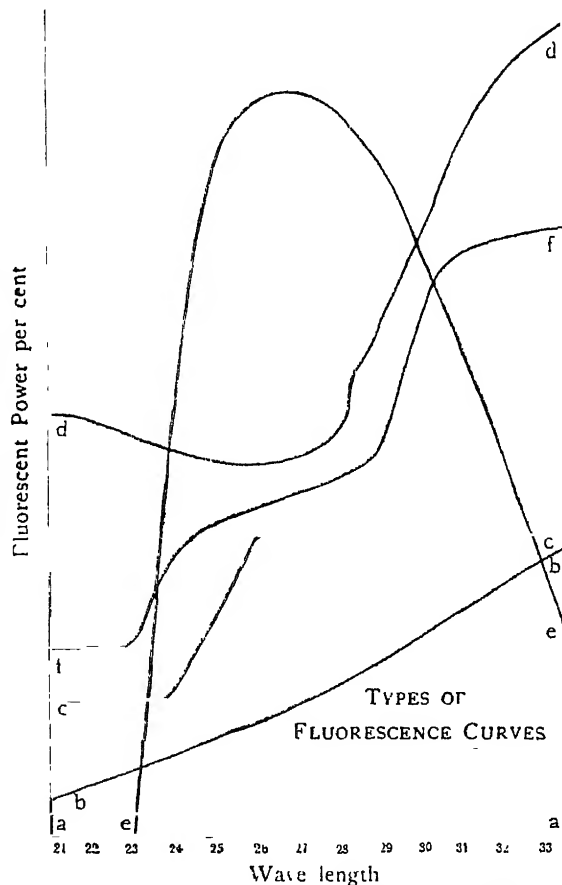

FIG. 49 —TYPES OF FLUORESCENCE CURVES
(Lewis)

Cotton and Copper Solutions.

An ammoniacal solution of cupric oxide known as Schweitzer's reagent, has long been known as a solvent for cotton and other forms of cellulose, and such solutions have long been employed for the production of artificial silk   The solvent power of such cuprammonium solutions varies with their composition and mode of preparation.   Three methods are therefore given here

  1 Gibson, Spencer and McCall (*Journ Chem Soc ,* 1920, cxvii. 492) prepare a satisfactory solution by dissolving 60 g. of copper sulphate in 1 litre of hot water
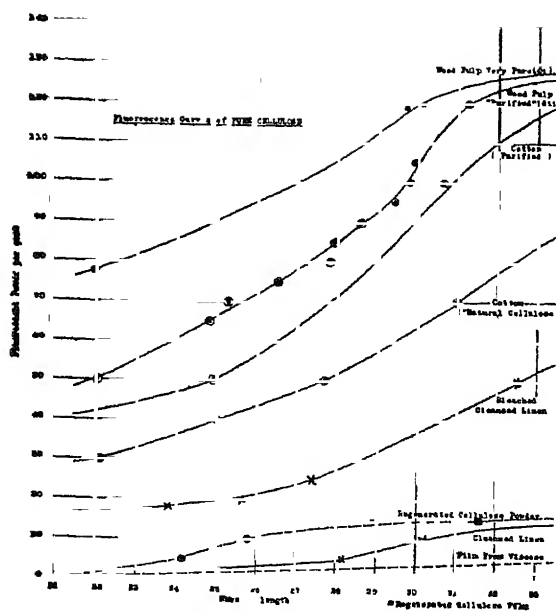
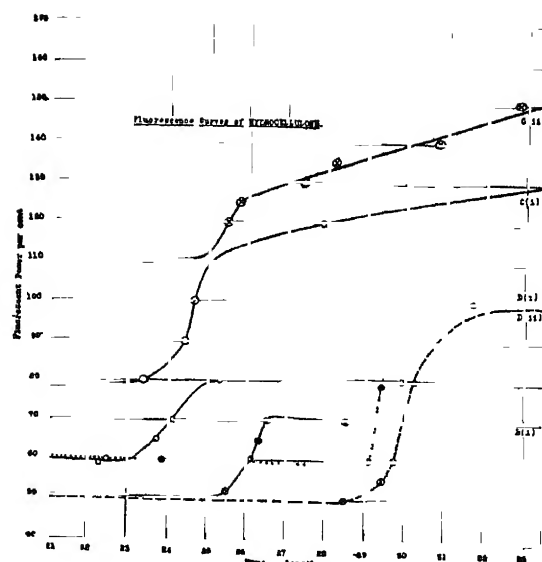FIG 50.—FLUORESCENT CURVES OF PURE
CELLULOSE
(Lewis.)

FIG 51 —FLUORESCENT CURVES OF OXYCELLULOSE
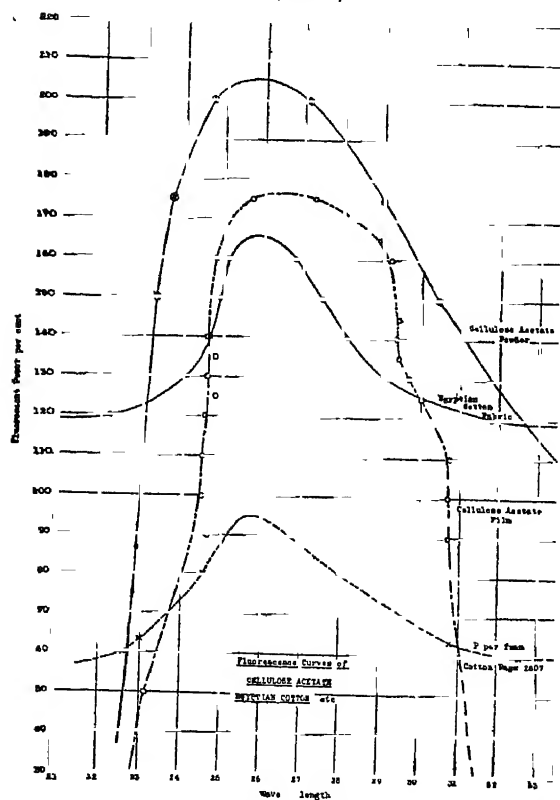AND HYDROCELLULOSE.
(Lewis.)

FIG. 52 —FLUORESCENT CURVES OF CELLULOSE
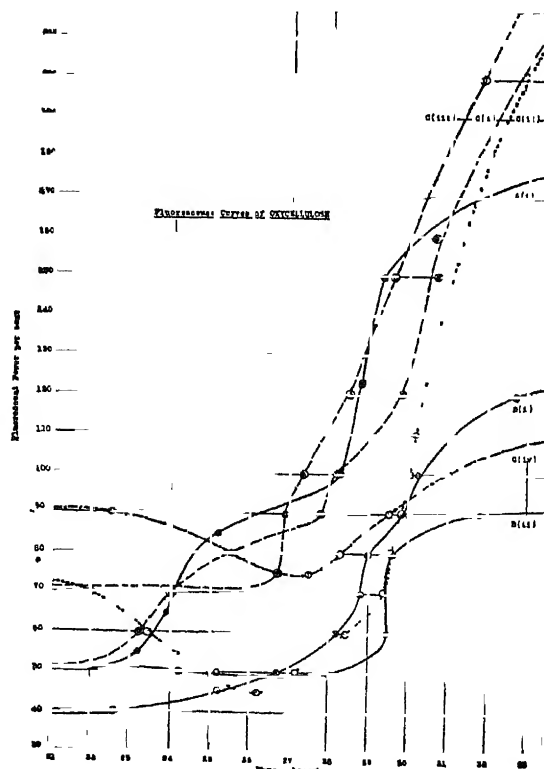DERIVATIVES.
(Lewis)

FIG. 53.—FLUORESCENT CURVES OF OXYCELLULOSE.
(Lewis)

containing a few drops of sulphuric acid, allowing the solution to cool to 50° C, and then adding 0·880 ammonia until the precipitation of basic copper sulphate is complete, sulphuric acid then being added to neutralise any excess of alkali The precipitate is washed with hot water by decantation, and then converted into blue cupric hydroxide by shaking it with 200 c c of 20 per cent caustic soda. Subsequently, the precipitate is washed by decantation with cold water until free from alkali and sulphate.

The precipitate is collected and dried on a porous plate at 40° C. and then well shaken with 800 c c of ammonia (containing 200–210 g. of ammonia per litre) After settling, the supernatant liquor is run off, and the copper content of the remaining suspension determined. The theoretical quantity of ammonia is then added to give a solution containing 11 g of copper and 200–210 g. of ammonia per litre

2 Joyner (*Journ Chem Soc*, 1922, cxxi 1512) simply bubbles air through a mixture of copper turnings and strong ammonia, ammonia or water being added to the product according to the strength desired. In this manner, solutions containing more than 30 g of copper per litre can be obtained. It was also found that the addition of a small amount of sucrose, about 1 g per litre, accelerated the dissolution of the copper. Such solutions appear to be quite stable, and one containing 36 g. of copper per litre (capable of dissolving 90 g. of cellulose per litre) remained unaltered during 3 weeks.

3. An electrical method is employed by Farrow and Neale (*Journ. Text. Inst*, 1924, xv 159). A tall glass cylinder contains a strong solution of ammonia and vertical copper electrodes, the cathode being in the form of copper tubing The whole is cooled by a water jacket. After the addition of 1 g. of sucrose per 1 litre of ammonia, the solution is electrolysed with a current density of 0·02 amperes, while oxygen, forced downwards through the cathode, rises upwards through the solution. After about 24 hours, the solution contains about 15 g. of copper in solution per litre and also a small amount (not exceeding 2 g. per litre) of nitrite.

Subsequently the solution is analysed and suitable additions of water or ammonia made to bring it to the desired strength

When cotton hairs are immersed in cuprammonium solution, they swell in the manner shown in Fig 1 (x), and ultimately dissolve, with the exception of the cuticle. Various observers state that unripe cotton hairs do not dissolve and do not swell Addition of water or solutions of electrolytes to cuprammonium solutions of cotton at once leads to precipitation of the cellulose, which is but a slightly different modification of the original cotton

Apart from their technical importance in the manufacture of artificial silks and the production of Willesden fabrics, such solutions of cotton are useful as affording evidence of the character of the cotton from which they have been prepared. Measurement of the viscosities of cuprammonium solutions of cellulose is, in fact, likely to become an important means of controlling textile

processes in bleaching and dyeing works, although investigations of this subject have been largely developed in connection with the conversion of cotton into guncotton.[1]

It should be noted here, however, that the resulting viscosities of the cotton solutions are dependent on the cuprammonium solutions employed. For instance, Joyner (*Journ Chem Soc.*, 1922, cxxi. 1511) notes that the logarithm of the viscosity of a cuprammonium solution of cellulose is directly proportional to the increase of ammonia concentration, and is independent of the viscosity either of the cotton, the amount taken, or the amount of copper in solution Low copper concentration tends to produce solutions having low viscosities, but there is a limit to the effect produced by the concentration of the copper, and this limit lies in the neighbourhood of 30 g per litre

Joyner further observes that 162 g. of cellulose requires about 70 g. of copper ($C_6H_{10}O_5/Cu$), and that when the ratio of copper to cellulose in solution is increased to three times this value, the least viscous solution of cellulose is obtained It also appears that the solubility of cotton in cuprammonium is dependent only on the copper concentration, provided that there is enough ammonia present, and is independent of the viscosity of the cellulose.

Cuprammonium solution readily absorbs oxygen from the air, and this absorption lowers the viscosity of cellulose solutions. Consequently, before this was noted, unreliable results were obtained Joyner (*supra*) found that when 2·7, 13·6 and 30 c.c of air were allowed to come in contact with 75 c c portions of a 2 per cent. cuprammonium solution of cellulose, the viscosities were lowered by 530, 1300 and 1800 seconds respectively. For this reason, the viscosity is best determined in an atmosphere of hydrogen.

Recently, Farrow and Neale (*Journ. Text. Inst.*, 1924, xv. 157) have devised a method (based on the technique of previous workers) for measuring the viscosities of cuprammonium solutions of cotton, and have described their results obtained in the examination of cotton before and after treatment with various reagents.

The solvent is prepared by the method described (*supra*) and contains about 15 g of copper and 240 g of ammonia per litre It is stored in a blackened bottle connected to hydrogen, so that changes promoted by light and air may be avoided

Experiment showed that the drying of cotton affects its viscosity. For example, cotton dried at 110° C for 24 hours had a viscosity of 45 as compared with 71 before drying

It is found that 2 per cent solutions of normal cottons are convenient to work with, and these are prepared by shaking (mechanically) 1 gram of the cotton with 50 c.c. of cuprammonium solution in an atmosphere of hydrogen Solution may take a few minutes or 1 or 2 days. The viscosities of these solutions is then determined by observing the times required for a steel ball to fall through them under standard conditions.

With two different qualities of cotton fabric it was found, as the results here given show, that the viscosity of the resulting cuprammonium solutions decrease generally with the severity of the treatment to which the fabrics were subjected.

TABLE LXXX

Process or Nature of Cloth	Log η of 2 per cent. Solution.	
	Quality 1.	Quality 2.
Grey	2·143[1]	..
Singed, steeped, caustic boiled, soured and washed	1·45	1 70
As above, then chemicked, soured and washed .	1·47	1·55
Singed, steeped, lime boiled, soured and washed .	2·00	1·48
As above, then ash boiled, soured and washed .	1·86	1·27
As above, then chemicked, soured and washed .	1·67	0·99
Singed, steeped, water boiled, soured, washed, caustic boiled and washed	1·85	1·77
As above, then chemicked, soured and washed .	1·62	1·49

η = Viscosity.   [1] Solution was incomplete

Some Egyptian Sakellaridis cotton yarn was untwisted and immersed in cold sulphuric acid of various strengths for 2 days, then thoroughly washed and air dried, the viscosities of their cuprammonium solutions being then compared with the tensile strengths of the individual fibres. The following results were obtained :

TABLE LXXXI

Acid Solution. Grams of H_2SO_4 per 100 c c	Log η	Mean Tensile Strength (100 hairs)	Probable Error.
0 . . .	2·275	4·55 g.	± 0·12
10	1·327	4·18	± 0 10
20	0·686	3·50	± 0·07
30	0·024	2·94	± 0 06
40	1̄·53	2 06	± 0·04
50	1̄·23	1·32	± 0·08
60	2̄·98	0·66	± 0 02
70 . . .	2̄·85	0·00	..

and the decrease of viscosity with decrease of tensile strength is evident.

Oxidation of cotton, with consequent reduction of its tensile strength, was also shown to produce lower viscosities, thus

TABLE LXXXII

OXIDATION WITH HYPOBROMITE

Per Cent Oxygen consumed in Oxidation of Cotton.	Log. η 2 per cent Solution	Hair Strength	Probable Error.
0·00 g	3·40	3·40 g	± 0·10
0·064	1·78	3·03	± 0·09
0·096	0 68	2·80	± 0·08
0·16	1·96	2 48	± 0·08
0 32	1·36	1·65	± 0·05
0 48	1·08	1 11	± 0·06

OXIDATION BY PERMANGANATE

0 00	3·40	3·4	± 0·10
0·032	2·39	..	..
0 064	1·86	..	..
0 096	1·84	..	..
0·139	1·35	3·15	± 0·09
0·192	0·747	2·98	± 0·10
0·304	1·86	2 91	± 0·09

The viscosity of cotton is not much affected by mercerisation.

It is concluded that the viscosity of a 2 per cent solution of a carefully bleached cloth should lie between 300 and 10 C G.S units (log η=2·5 to 1·0), and that determination of such viscosity enables mechanical damage of cotton materials to be distinguished from chemical attack

In their experiments on the tendering of cotton fabric (see page 106) Coward, Wood and Barratt compared the degree of tendering with loss of viscosity A series of samples of cotton fabrics tendered by heating with hydrochloric acid between heated copper plates were employed and the results shown in Fig 54 It is noted that the viscosity of the tendered fabric is a much more sensitive indication of the first stages of tendering than is the tensile strength. Thus when the strength of the fabric is reduced 10 per cent., the loss of viscosity is 60 per cent.

Alkaline solutions containing copper are also useful since they are capable of being reduced by degraded cellulose Thus when overbleached cotton is heated with Fehling's solution (see page 217) a red precipitate of cuprous oxide is formed, under similar conditions pure normal cellulose does not produce this precipitate.

Generally it is found that cellulose, which has been degraded by treatment with acids, oxidising agents, heat or the like, is able to reduce an amount of cupric hydroxide approximately proportional to the degree of its degradation Hence methods have been devised, and they are described in more detail later (see page 216), whereby the exact reducing power of degraded cotton may be determined under standard conditions. In this manner, a *copper number* can be assigned to any type of degraded cotton, and it indicates the amount of copper which 100 g of that cotton can reduce. Pure cellulose should have a copper number o, whereas some degraded celluloses have been found to have a copper number of 14.

That the copper number of cellulose is a reliable index of the degree to which that cellulose has been oxidised is supported by some experiments of Knecht and Thompson (*Journ. Soc Dyers & Col*, 1922, xxxviii. 132). These workers oxidised cotton yarn to a measurable extent by means of potassium permanganate and sulphuric acid (see page 151) and then determined the copper numbers of resulting yarn. They obtained the following results :

TABLE LXXXIII

Degree of Oxidation of Yarn. o per $C_6H_{10}O_5$.	Copper Number.
1 atom	14·0
$\frac{3}{4}$,,	13·2
$\frac{1}{2}$,,	12·7
$\frac{1}{4}$,,	9·1
$\frac{1}{8}$,,	7·2
$\frac{1}{12}$,,	6·6
$\frac{1}{16}$,,	5·3
Nil	0·6

Cotton and Water.

The behaviour of cotton towards water and water vapour is of considerable importance in textile industry, but it has received comparatively little systematic investigation. Generally, it is considered that cotton suffers no deterioration when maintained in a wet state, provided that no bacteria or catalysts are present. But when subjected to digestion with boiling water, cotton is affected to a small extent.

Extraction of raw cotton with cold or warm water removes most of its phosphorus content, a small proportion of nitrogen and a constituent which has a high hygroscopic power.

Tauss (*Dingler's Poly. Journ.*, 1889, cclxxiii. 276 ; 1890, cclxxvi. 411) heated

Swedish filter paper with fifty times its weight of water under 1–20 atmospheres pressure, and obtained extracts having reducing power and capable of giving a red colour with phloroglucinol and hydrochloric acid. Some of his results are given here

TABLE LXXXIV

Pressure	Amount of Extract.				Sugar in Extract (calculated as Dextrose).			
	1st Boil.	2nd Boil	3rd Boil	Total	1st Boil.	2nd Boil	3rd Boil	Total.
5 atm	0·74%	0·40%	0·24%	1·38%	0·10%	0·01%	0·01%	0·12%
10 atm	9·44%	3 84%	0·20%	13 5%	3·90%	1 50%	0·10%	5·50%

Under 20 atmospheres, the cotton was converted into a jelly-like mass

Subsequently, Schwalbe and Robinoff have shown that pure cellulose is only slightly attacked when heated with water under 20 atmospheres pressure, but cotton which is impure or has been previously bleached is attacked. For instance :

TABLE LXXXV

Cellulose.	Copper Number after heating with Water at								
	20° C.	100° C	105° C	120° C	135° C	150° C	165° C	179° C.	213° C.
Before bleaching .	0·04	0·11	0·11	0·13	0·15	0·19	0·26	0 30	..
After bleaching .	0·37	0·31	..	0·33	0·40	0·48	0·43	1·80	3·40

The steaming of cotton frequently results in a darkening of colour, and this is more pronounced as the cotton contains a greater amount of pectic substances or oxycellulose.

More recently, Huebner and Kaye (*Journ. Soc. Chem Ind.*, 1922, xlii 94) have found that when highly purified cotton is steeped in water at 35° C for a considerable time, soluble aldehydic substances may be detected in solution by the usual tests. Similarly, when cotton is submitted to steam distillation, aldehydic substances may be detected in the distillate. Even more remarkable is the fact, that if cotton is placed over distilled water in a closed vessel for several days,

the water, without having come in contact with the cotton, acts as a weak solution of an aldehyde

When cotton is steeped in a solution containing sodium acetate at 35° C. for a few days, the amount of aldehyde produced is so considerable that it can be readily separated by distillation. At the same time, it was shown that when cotton is placed in water, there is a contraction in total volume and a rise of temperature.
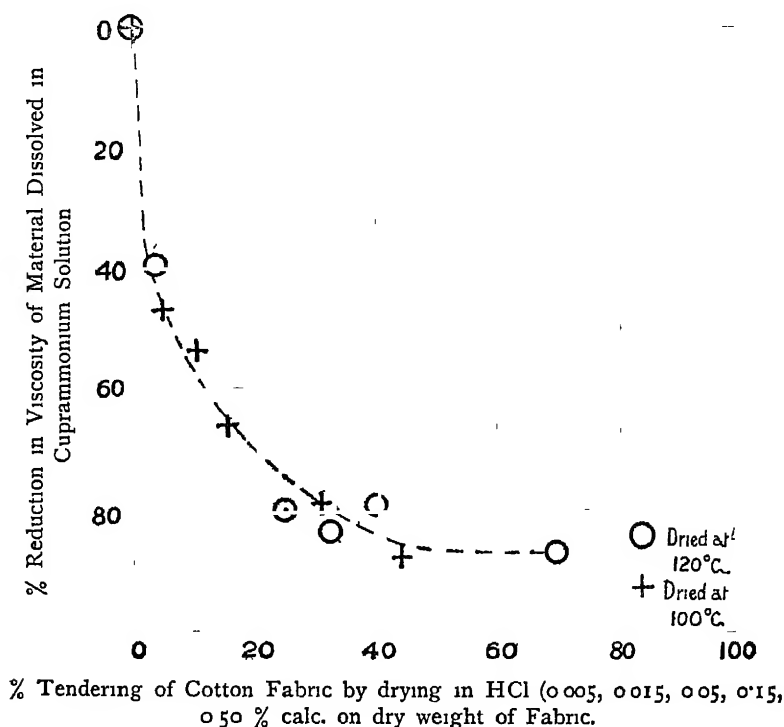
Later, Clifford and Fargher (*Journ. Text. Inst.*, 1923, xiv 122) have examined

% Tendering of Cotton Fabric by drying in HCl (0 005, 0 015, 0 05, 0·15, 0 50 % calc. on dry weight of Fabric.

FIG. 54.—VISCOSITIES OF TENDERED COTTON FABRIC.
(Coward, Wood and Barratt)

the products obtained by the action of water heated at 40 lb. pressure on cotton. These products included acetaldehyde, acetone, traces of an aldehyde or ketone yielding a *p*-nitrophenylhydrazone m p. 109°–110° C , ammonia and traces of trimethylamine. No methyl alcohol was detected, but it was shown that the aqueous extract yielded a pectin substance which gave methyl alcohol and traces of acetone when heated with caustic soda

Coward and Spencer (*Journ. Text Inst.*, 1923, xiv 28) show that when scoured loose cotton is wetted out with water and centrifuged so that all inter-

fibrillar water is removed, 100 g. of cotton retains about 50 per cent. of water, which is most probably distributed throughout the cellulose of each cotton hair.

Recently, Urquhart and Williams (*Journ. Text Inst*, 1924, xv. 138) have investigated the moisture absorption and desorption of cotton when exposed in atmospheres of different humidities

American cotton was used, both in sliver form and after kiering for 10 hours at 40 lb. pressure in caustic soda of initial concentration of about 1·7 per cent. and final concentration 1·2 per cent., the results being further classified according as

Absorption and Desorption of Water at 20°C.
by Raw Cotton 85R, Dried at 15°C.

Absorption Curve ———o———

Desorption Curve ———a———
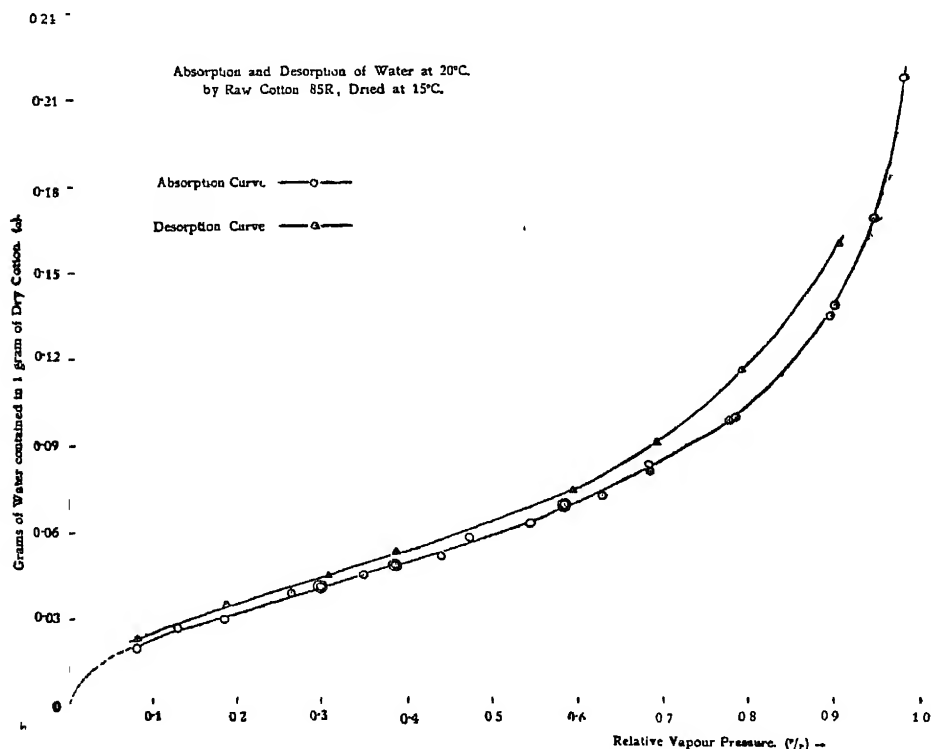
FIG. 55 —ABSORPTION AND DESORPTION OF WATER BY RAW COTTON AT 20° C.
(Urquhart and Williams.)

the cotton before testing was dried at 15° C. over phosphorus pentoxide, or at 110° C

It was shown that raw cotton suffers a greater loss of weight when dried at 110° C. than at 15° C., but this difference is not evident with kiered cotton. Hence, it seems probable that drying at the higher temperature removes a non-cellulosic constituent from raw cotton which is not present in kiered cotton. This constituent is evidently hygroscopic since kiered cotton takes up less moisture than raw cotton under the same conditions.

In these experiments, the samples of cotton were moved through atmospheres of increasing and then decreasing humidity, their moisture contents being determined at various humidities.   The results obtained with raw and kiered cottons dried at 15° C. are expressed in Figs. 55 and 56, and it is evident from these curves and the other results obtained that when a sample of cotton is exposed to an atmosphere of given temperature and humidity, there are at least two possible values for the resulting moisture content of the cotton, according as it absorbs or desorbs moisture.   The hysteresis observed by Kujirai, Kobayashi and Toriyama (*Journ. Soc. Chem Ind*, 1923, xlii. 894A) is thus confirmed

In some earlier experiments by Masson and Richards (*Proc Roy Soc.*, 1906, lxxviii 412) this hysteresis, shown by the following results, was attributed to a lag in the attainment of equilibrium; but this explanation, in view of the investigations of Urquhart and Williams (*supra*), is probably not correct.

TABLE LXXXVI

Relative Vapour Pressure .	0·100,	0·294,	0·500,	0·710,	0·952,	0·972

Grams of water absorbed by 0·984 g of dry cotton	Cotton originally dry	0·0175,	0·0356,	0·0509,	0·0716,	0·1378,	0·1563
	Cotton originally wet	0·0198,	0·0406,	0·0593,	0·0840,	0·1606,	0·1792

Cotton therefore behaves as a colloidal mass of cellulose, having a moisture content dependent on the humidity of the surrounding atmosphere, but usually about 7 per cent.

Cotton and Bacteria.

It has long been recognised that cotton is susceptible to attack by fungi and moulds, but not until recently has it been discovered that cotton may be rapidly attacked by bacteria   In fact, owing to the demand for the production of alcohol from cellulosic materials, it seems likely that the selection and cultivation of bacteria capable of decomposing cellulose will be of considerable importance.

Forty years ago, Hoppe-Seyler was able to convert about 26 grams of filter paper solely into marsh gas and carbon dioxide during 4 years by the action of organisms found in sewer mud   Subsequently Omelianski (cf. " Fermentation," *Thorpe's Dictionary of Chemistry*) found evidence that cellulose is attacked by two types of anaerobic bacteria present in sewer mud or manure, one type being capable of producing hydrogen and the other, methane   Under conditions such

that the growth of one or other of these bacteria was favoured, Omelianski obtained the following quantitative results with pure cellulose

<div align="center">TABLE LXXXVII</div>

Product of Decomposition	Hydrogen Fermentation.	Methane Fermentation.
Carbon dioxide . .	29·1 per cent	43·2 per cent.
Hydrogen . .	0·4 ,,	..
Methane . .	..	6·8 ,,
Acetic acid . . .	35·9 ,,	43·6 ,,
Butyric acid	31·0 ,,	7·1 ,,
Totals . .	96·4 ,,	100 7 ,,

Acetic and butyric acids are products formed in both types of fermentation.

The high proportion of methane sometimes found in the air of wooded districts (Gautier found in one instance, 11·3 c c. per 100 litres) is probably due to such fermentation

Bacilli isolated from human intestines have been shown capable of decomposing cellulose. On the other hand, Pringsheim and Markatz (*Zeit. physiol. chem.*, 1919, cv 173–178) have found that diastase and extracts from the stomach, intestines and pancreas of oxen were unable to decompose a dextrin prepared from cellulose.

At Rothampstead, Hutchinson and Clayton (*Journ Agric. Sci.*, 1919, IX. 143–173) have obtained a culture from the soil, *Spirochæta cytophaga*, which rapidly decomposes cellulose at 25°–30° C. under aerobic conditions, thereby producing a mucilage of a pectin character

Norbet von Gescher (*Faserforchung*, 1922, II. 28–40) gives a detailed account of the action of cellulose destroying bacteria on cellulose, oxycellulose, hydrocellulose, starch, sucrose, maltose, glucose and cellobiose. Such bacteria thrive on cellulose, oxycellulose and hydrocellulose but not on the other carbohydrates.

More recently, Cross and Doree (*Researches on Cellulose IV*) are able to quote some results obtained in the commercial fermentation of cellulosic materials by Power Spirits Ltd., for the production of alcohol. Certain organisms, which are not described, are stated to be capable of completely destroying cellulose within 24–28 hours. By control of the conditions, the end products may be varied so as to yield :

1. Alcohol and acetic acid ; hydrogen and carbon dioxide.
2. Acetic acid ; methane and carbon dioxide.
3. A mixture of products in 1 and 2.

It is also noticed that the carbon dioxide is always contaminated with hydrogen or methane or a mixture of these, and that the production of alcohol is always accompanied by acetic acid. The products of fermentation frequently weigh more than 110 per cent. of the cellulose fermented

Under conditions not specified the following results were obtained by fermentation of wood cellulose sulphite pulp :

TABLE LXXXVIII

Acetic acid .	.	.	31·8 per cent.
Lactic acid .	.	.	9·6 ,,
Alcohol	.	.	27·6 ,,
Carbon dioxide	.	.	42·4 ,,
Hydrogen .	.	.	1·0 ,,
Methane	.	.	0·2 ,,

Fleming and Thaysen (*Biochem. Journ.*, 1920, xiv. 25 and 1921, xv. 407) and Thaysen (*Journ. Soc. Dyers & Col*, 1924, xl. 101) have also investigated the action
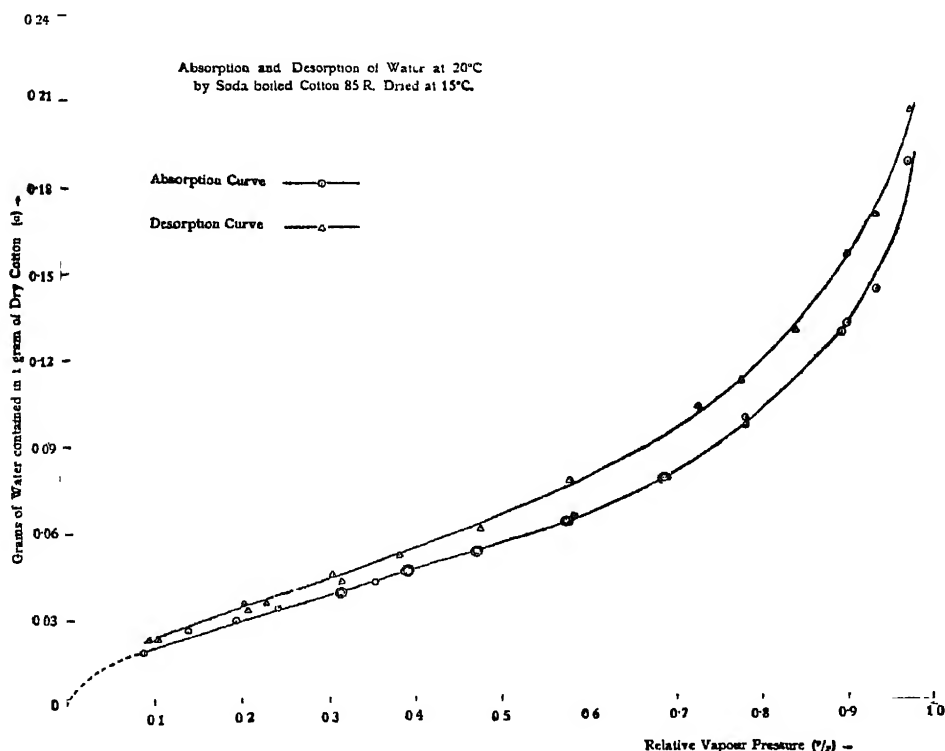
FIG 56.—ABSORPTION AND DESORPTION OF WATER BY SODA-BOILED COTTON AT 20° C.
(Urquhart and Williams)

of various bacteria and moulds on cotton. They showed that cotton stored in a damp condition is deteriorated by the attack of a streptothrix and a schiozomycete, the cuticle being destroyed. This destruction of the cuticle is utilised as the basis of a method for quantitatively measuring the degree of bacterial attack, though Denham (*Journ Text. Inst*, 1923, xiv. 143) criticises its accuracy.

In this method, the cotton fibres (0·1 g.) are boiled in 1 per cent. caustic soda, soured with acetic acid, washed and steeped in 1·5 c c. of 15 per cent. caustic soda, and afterwards 1·5 c c. of carbon bisulphide are added. The fibres, after 15–45 minutes, are then examined under the microscope, when a normal fibre shows a characteristic bulb-like swelling, while a fibre whose cuticle has been attacked by bacteria swells uniformly (see Fig 57) By counting, the proportion of attacked fibres can be estimated.

Fleming and Thaysen state that a good Indian cotton may contain about 1·5 millions of bacteria per gram, most of which appear to be derived from soil.
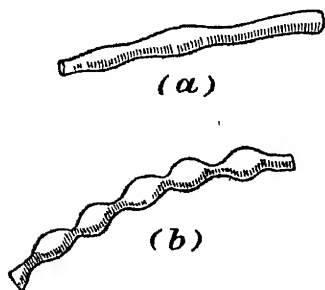
FIG 57

(*a*) FIBRE ATTACKED BY BACTERIA
(*b*) NORMAL FIBRE.

After swelling in Carbon Bisulphide
and Caustic Soda
(Thaysen)

Moisture has a large effect on the attack of cotton by both bacteria and fungi. For instance, Fleming and Thaysen found that when cotton containing 1·4 million of bacteria was maintained for 3 days at 16° C. in the presence of 6–9 per cent. of moisture, there was no increase in its bacterial content; when the moisture was increased to 10, 15, 20 and 50 per cent., the bacteria increased to 124, 499, 1112 and 9040 millions respectively.

It is also interesting to find that Doree (*Biochem. Journ.*, 1920, xiv. 709) considers that when cotton materials are immersed in sea water, their disintegration is largely due to bacterial attack in the presence of oxygen. Doree found that cotton and linen fabrics were completely tendered after 3–5 weeks' immersion in sea water, and some bleached cotton yielded the following results after 3 weeks' exposure ·

Loss of weight in boiling 1 per cent. caustic
    soda (5 minutes) .   .   .   .   . 17·44 per cent.
Loss of weight in boiling 1 per cent. caustic
    soda (60 minutes)   .   .   .   . 17·70   ,,
Loss of weight in cold 17·5 per cent. caustic
    soda (20 minutes)   .   .   .   . 19·15   ,,
Copper number .   .   .   .   .   . 1·42   ,,

Cellulose triacetate, in which the hydroxyl groups are not free, was found to be unattacked after immersion in sea water for 6 months.

Although fungi are capable of growing on pure cellulose, such growths, in technical practice, are usually met with on cotton fabrics which also contain starchy sizing materials, and for many years textile manufacturers have been obliged to counter mildew attacks by means of suitable antiseptics. Such difficulties of mildew are dealt with in an early book by Davis, Dreyfus and Holland (*Sizing and Mildew in Cotton Goods* ; Manchester, 1880).

Generally, it is found that all kinds of cotton goods are contaminated with spores of various fungi, and that under favourable conditions of humidity and temperature development of these spores occurs more or less rapidly, the mycelia of the fungi penetrating the fibre walls thereby producing serious damage, while the growth is sustained probably by dextrins which are produced by the action of enzymes (secreted by the growing fungi) on the cellulose.

Tabulated results obtained by Williams (*Journ. Soc. Chem Ind.*, 1891, x. 227) during an investigation of the action of mildew on thirty samples of fabric, some of which contained definite amounts of various antiseptics, indicate that under favourable conditions mildew occurred within 44–126 hours, but that the presence of zinc chloride certainly resisted mildew attack

Osborne (*Journ Soc Dyers & Col*, 1912, xxviii 204) describes various moulds and mildews found on cotton fabrics and summarises methods for their identification and the most favourable conditions for their growth His results obtained in examination of various samples of mildewed fabrics are tabulated thus :

TABLE LXXXIX

Sample of Material	Damage Observed	Organisms identified on Fabric approximately in the Order of Predominance
Flour size	Fermenting	Anaerobic bacteria
Grey cloth.	None	Bacteria only
Grey cloth.	Black line along one fold, black, pink and yellow spots	*Penicillium, Mucors (M racemosus* and *M. spinosus), Fusarium,* bacteria
Grey cloth.	Numerous black, red and yellow spots	*Fusarium, Mucors (M racemosus), Penicillium,* bacteria.
Coarse cloth with much size	Brown stains	*Penicillium,* brown *Torula, Erotium sp, Aspergillus niger,* few bacteria
Khaki drill	Lighter spots	Bacteria only
Cotton cops	Outer threads dirty grey.	*Fusarium,* various *Hyphomycetes,* few bacteria

In a preliminary description of work relating to the establishment of methods

for determination of the resistance of fabrics to attack by mildew, Levine and Veitch (*Journ. Ind. Eng. Chem.*, 1920, xiii 139) state that cotton goods are most frequently attacked by *Alternaria*, *Aspergillus*, *Claudisporium* and some *Mucors*. Pink stains on fabrics are often due to the presence of a *Mucor* and a mould capable of producing a substance having a pink colour in alkaline or neutral media and yellow in acid media. It was also found that canvas could be completely destroyed by *Aspergillus*, and that cotton buried in the soil is subject more to bacterial rather than fungoid attack

Corrigan has collected some useful information concerning the influence of bacteria and moulds on vegetable fibres, and mentions (*Journ Soc. Dyers & Col.*, 1920, xxxvi. 198) copper sulphate, potassium nitrate, zinc sulphate, zinc chloride, formaldehyde and boric acid as antiseptics used in the finishing and sizing of cotton goods.

Examination of printed cotton cloth wrapped on board by Sidebotham (*Journ Soc. Dyers & Col.*, 1922, xxxviii 97) showed that such cloth was attacked by a fungus (*Botrytis*) which was originally present in the subcortical part of the wood This fungus was found to grow equally well in the dyed and undyed portions of the cloth and most rapidly at a temperature of 90°–100° F.

More recently, some interesting facts relating to mildew have been observed by Armstead and Harland (*Journ. Text. Inst*, 1923, xiv. 339) in their examinations of some mildewed black-bordered dhooties. In this instance, the attack was independent of the size present, but was caused by a species of mould which could attack pure yarn having a relatively low content of moisture. The attack resulted in the formation of black streaks and smudges.

In the first place, it was found useful to stain the fabric with Cotton-blue as a means of showing the extent of attack. The mycelia of fungi present are thus stained a darker blue than the associated cotton hairs. Subsequently, growth of the mould on the fabric was encouraged by placing portions of the fabric in sterilised Petri dishes in a desiccator over water, and the mould was then identified as produced by a *Penicillium* and *Aspergillus niger* The latter could not be grown on the black border of the fabric, and this is obviously an example where a dyestuff inhibits the growth of mould.

In further experiments, the influence of moisture on the growth of *Aspergillus niger* on fabric was shown as in Table XC

It is concluded that when a fabric is infected with spores of *Aspergillus*, and maintained so that its moisture content is about 8 per cent., fructification will occur within 9 weeks and a typical mildewed appearance ensue. With a higher moisture content, the development will be much more rapid, but with a moisture content, not exceeding 7 per cent., mildew is not likely to develop.

The vapours of naphthol, naphthalene, thymol and formalin were found to prevent mildew considerably.

It therefore appears that cotton is by no means so immune from bacterial and fungoid attack as was at one time thought to be, and that the presence of

moisture favours such attacks. Since acetylated cellulose is almost immune, it would be probable that cuprammonium and viscose artificial silks are more susceptible to bacterial and mildew attack than ordinary cotton.

TABLE XC

Moisture Content of Fabric	Growth of *Aspergillus*.
15 5 per cent	Profuse (after 14 days).
14·8 ,,	,, ,, ,,
12·8 ,,	Very little (6 weeks)
14·8 ,,	Profuse (6 weeks)
7·8 ,,	Moderate growth (9 weeks)
7·0 ,,	None (after 4 months)

CHAPTER VI

CELLULOSE AND OXIDISING AGENTS

SOME forty years ago Witz (*Bull. Soc. Ind Rouen*, x. 5, 416) first drew attention to the definite action of oxidising agents upon cellulose when investigating some fabrics which had been tendered in a bleaching works   At about the same time, Cross and Bevan visited Witz, and subsequently the term oxycellulose was coined to denote cotton modified by oxidation.   Since that time, oxycellulose has not been shown to be a definite chemical compound and the name is therefore somewhat misleading.   In this book the term oxycellulose, where used at all, must be considered as meaning the insoluble portion of the product (probably a mixture of substances) obtained by oxidation of cotton or other cellulose

Oxidised cellulose was soon shown to have properties quite distinct from those of pure cellulose.   For instance it resists dyeing with direct cotton dye-stuffs, and has an increased affinity for basic dyes such as Methylene Blue. It is more soluble than cellulose in caustic alkalis, and has greater reducing power.

At first oxycellulose was regarded as being a definite chemical compound. Thus Cross and Bevan (*Journ. Chem. Soc.*, 1883, xliii. 22) boiled cotton with 60 per cent. nitric acid whereby it was slowly converted to oxalic acid and an insoluble product—oxidised cellulose   About 30 per cent. of oxidised cellulose, calculated on the original weight of cotton, was obtained, and this was shown to be soluble in caustic soda from which it could be precipitated with acids or saline substances   The reprecipitated product had a composition agreeing with $C_{18}H_{26}O_{16}$, and on nitration it yielded a compound having the composition indicated by the formula—$C_{18}H_{23}O_{16}(NO_2)_3$

The oxycellulose thus obtained dissolved in concentrated sulphuric acid with a pink colour, but gave no colour with iodine

Subsequently these same workers (*Journ. Soc Chem Ind*, 1884, iii. 206, 291) oxidised cellulose with alkaline potassium permanganate till it was completely dissolved.   From the solution, by means of lead acetate, a lead salt of a gummy product was obtained and shown to have the composition $C_{19}H_{18}O_{22}$ Meanwhile Witz had shown that the action of bleaching powder solutions on cellulose was considerably increased when exposed to light and carbon dioxide. Further, Witz and Osmund (*Bull Soc Chim*, 1886, xlv 309) showed that oxidised cellulose was able to absorb vanadium from very weak solutions of its salts   When oxidised cotton was steeped in a solution containing 0·1–0·000001 mg of vanadium per litre and subsequently impregnated with aniline chloride and sodium chlorate and heated, it readily became black owing to the vanadium having catalytically promoted the oxidation of the aniline

Since these early investigations, the oxidation of cellulose by almost all

possible oxidising agents has been studied, but no satisfactory conclusion as to its chemical structure has yet been reached.

Vignon (*Compt. rend*, 1897, cxxv. 448; 1898, cxxvi. 1355) found that cotton is readily oxidised by the action of hydrochloric acid and potassium chlorate. Under certain conditions, the oxidised product was 40 per cent. soluble in 28 per cent. caustic potash, and by addition of acid only part of the soluble portion was reprecipitated.

Cross, Bevan and Beadle (*Ber*, 1893, xxiii. 2527) also investigated the action of chromic acid on cellulose and cellulosic materials. They found that after oxidation, cellulose gave a greater yield of furfurol when distilled with hydrochloric acid of sp gr. 1·06. Some normal alkali-boiled and bleached cotton was oxidised with varying amounts of chromic acid, and the yields of furfurol from the oxidised insoluble product determined. Some results obtained were :

<div align="center">TABLE XCI</div>

Weight of Cotton	Amount of CrO_3.	Weight of Oxidised Cellulose.	Yield of Furfurol.
4·7 g.	1·5 g	93·0 per cent.	4·1 per cent.
4·7	3·0	87·0 ,,	6·3 ,,
4·7	4·5	82·3 ,,	8·3 ,,
Untreated cellulose			0·2 ,,

By more drastic treatment, cotton may be completely oxidised by means of chromic acid to carbon dioxide and water (see page 220)

Faber and Tollens (*Ber.*, 1899, xxxii. 2589) have found that bromine is not very active as an oxidant for cotton ; some oxidised products examined yielded 1·4–1·8 per cent. of furfurol when distilled with hydrochloric acid of sp. gr. 1·06.

Oxidants of the peroxide type, such as hydrogen peroxide, sodium perborate, potassium persulphate and ozone, have also been found to oxidise cellulose yielding products similar to those obtained by other oxidising agents.

Ditz (*Chem. Zeit*, 1907, xxxi. 833) describes the action of acidified solutions of a persulphate on cotton. It was found that when 2 g. of filter paper was heated at temperatures not exceeding 80° C. in a 10 per cent. solution of ammonium persulphate, to which had been added 1 c.c. of 20 per cent. sulphuric acid, evolution of gas occurred to a much greater extent than when cotton was absent. When the treated cellulose was afterwards washed with cold water, it was found to have the properties of a peroxide, and behaved similarly to the oxidised product obtained by Cross and Bevan (*Zeit angew. Chem*, 1906, xix. 2101). When immersed in an aqueous solution of potassium iodide it liberated iodine which could be readily detected by means of starch.

This cellulose peroxide was comparatively stable at ordinary temperatures, but was decomposed when immersed in boiling water.

When cellulose was heated to 100° C. in the acidified solution of ammonium persulphate, there was a vigorous evolution of oxygen and carbon dioxide, and it was evident that at this temperature the cellulose peroxide initially formed was immediately further decomposed

Kolb (*Bull. Soc Ind Mulhouse*, 1868, xxxviii. 914) and Vignon have studied the action of ozone, but more recently Doree and Cunningham (*Journ Chem. Soc.*, 1912, ci. 497) have investigated this action more fully

Some cotton-wool was sprayed with water and then treated in subdued light for 30 hours with a current of air containing 1·4 per cent of ozone. The product was white in colour, but became light brown when dried at 100° C. In water it swelled, but on drying it disintegrated It appeared readily susceptible to moulds and the action of acids and light. Further, the product was soluble in caustic potash, but no precipitate was obtained on addition of acids. It readily reduced Fehling solution, but not an ammoniacal solution of silver nitrate. Some results indicating the profound change produced by the action of ozone are given below ·

<div align="center">TABLE XCII</div>

		Original Cotton	Ozonised Cotton
Composition { Carbon . . .		44·44 per cent	43·55 per cent.
{ Hydrogen . .		6·17 ,,	6·27 ,,
Moisture		6·0 ,,	7·45 ,,
Furfurol (by HCl distillation) .		0·62 ,,	1·10 ,,
Methylene Blue absorption . .		0·56 ,,	2·96 ,,
Copper number		..	14·96 ,,
Soluble in KOH		..	64·2 ,,

Evidence was obtained that cellulose treated with ozone formed a cellulose peroxide capable of liberating iodine from potassium iodide The peroxide was insoluble in water, stable at ordinary temperatures, but decomposed at 80° C

Cellulose and Potassium Permanganate.

A considerable number of interesting facts concerning the oxidation of cellulose have been obtained by using potassium permanganate as an oxidising agent At one time, bleaching of cotton materials with this substance was carried out more extensively than it is to-day, and over-bleaching was frequent.

Quite early, Cross and Bevan (*Cellulose*, p 62) have recorded the effects of alkaline permanganate on cotton (see also page 152). These workers added 50 g.

of potassium permanganate in small portions at a time to 22·6 g of cotton in 400 c.c. of a caustic soda solution at 40°–50° C. The products of the oxidation $(2C_6H_{10}O_5/7O)$ were found to be .

TABLE XCIII

Oxidised cellulose . . . . . . 10·5 g =50 per cent
Oxidised carbohydrates in solution . 3·5 =16 ,,
Oxalic acid . . . . . 4·3 =20 ,,
Carbon dioxide, water, and traces of
    volatile acids . . . . . 0 7 =14 ,,

More recently Knecht and Thompson (*Journ. Soc. Dyers & Col*, 1920, xxxvi. 251) have oxidised cellulose under carefully controlled conditions by means of permanganate in the presence of sulphuric acid.

In the first place, it was ascertained that when cellulose was steeped in sulphuric acid of 10° Tw (sp. gr. 1·05) for a period of about 4 hours, it was not appreciably modified Then, in one particular experiment, 30 g of filter paper were suspended in 600–900 c c of 10° Tw. sulphuric acid and stirred continuously, while 12 g of potassium permanganate, also dissolved in 10° Tw. sulphuric acid, was added gradually during 1–2 hours Within 4 hours the permanganate was completely decolourised and a brown, finely divided product obtained This was filtered off, suspended in dilute sulphuric acid and decolourised by the careful addition of a solution of hydrogen peroxide, and the product afterwards filtered whereby a perfectly white residue of oxidised cellulose was obtained. Under these circumstances, where $C_6H_{10}O_5/1O$, the yield was equal to 94 5 per cent., calculated on the weight of original cellulose.

This oxidised cellulose was then carefully investigated

The oxidised cellulose was not soluble in a mixture of concentrated sulphuric and nitric acids, thus differing from that of Cross and Bevan (see page 148). It had no affinity for acid dyes, but an increased affinity for basic dyes such as Methylene Blue

The reducing and aldehydic properties of this oxidised cellulose were marked Thus it at once developed a deep magenta colour with Schiff's reagent, and formed a hydrazone with *p*-nitrophenylhydrazine.

When immersed in cold 5N caustic soda it at once gave a deep yellow colour ; the same colour was developed when the oxidised cellulose was boiled with N/100 caustic soda The colour was less readily developed by sodium carbonate solutions.

It would appear that, when the oxidised cellulose is treated with caustic soda, it undergoes simultaneous oxidation and reduction in much the same manner as does benzaldehyde

$$C_6H_5CHO + 2NaOH = C_6H_5COONa \quad C_6H_5CHONa + H_2O$$

Benzaldehyde   Benzoic Acid.   Benzyl Alcohol.
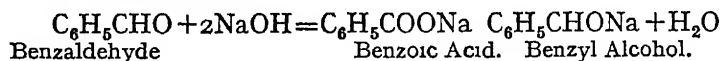
whereas the portion insoluble in alkali has no reducing properties and behaves like ordinary cellulose except that it is dyed by Methylene Blue, the portion precipitated from the alkali solution, on addition of acid, has only very slight reducing properties, but a strong affinity for Methylene Blue.

Subsequently, a more highly oxidised product—$C_6H_{10}O_5/2O$—was prepared with an average 93 per cent. yield. This oxidised cellulose had the same reducing and other properties, though more marked, as that previously prepared Efforts to conclusively prove that it contained an aldehyde group were not successful, though evidence was obtained. Thus, on treatment with ammonia 0·880, part of the oxidised cellulose combined with a small amount of ammonia. It also absorbed large quantities of sulphite from a concentrated solution of sodium bisulphite, and when 2 g of the oxidised cellulose were immersed in 25 c c. of 60° Tw. sodium bisulphite solution, the temperature of the mixture increased by 2·8° C According to this, if the oxidised cellulose were assumed to have a molecular weight $C_6H_{10}O_5$, the calorific heat of the reaction would be 7500 cals. Immersion of the oxidised cellulose in solutions of sodium bisulphite weaker than 50° Tw resulted in no temperature rise.

Such oxidised cellulose easily reduced ammoniacal solutions of silver nitrate and solutions containing cupric thiocyanate. It also reduced a solution containing ferric ferricyanide, so that a precipitate of Prussian Blue was formed.

In the presence of caustic soda, it was able to reduce ferric oxide to ferric hydroxide, and potassium ferricyanide to ferrocyanide. It was shown later, however, that pure cellulose was slowly oxidised in the cold by alkaline potassium ferricyanide

These strong reducing powers of oxidised cellulose are further shown by its behaviour with dyestuffs in the presence of alkali. Thus, a dilute solution of Methylene Blue containing a small amount of caustic soda is readily decolourised on the addition of oxidised cellulose. Similarly, direct dyes such as Rosinduline are reduced. Indigo can be reduced to form a solution capable of dyeing ordinary cotton

Rosinduline is a dyestuff which is stable to boiling caustic soda, and Knecht and Thompson therefore endeavoured to use this dye in the quantitative measurement of the reducing power of oxidised cellulose This was carried out by heating 0·3813 g of air-dry oxidised cellulose for 15 minutes with 40 c.c of 10 per cent. caustic soda and 100 c c. of a solution of Rosinduline G The dark-red solution was then acidified with tartaric acid, and the reduced dyestuff determined by titration with titanous chloride. It was shown in this manner that the copper number obtained was in fairly good agreement with that determined by other standard methods

It was further found that when the oxidised cellulose was heated with pure p-nitrophenylhydrazine, 100 g. of the cellulose absorbed about 56·1 g. of the hydrazine. Repeated washing of the product continuously removed hydrazine, so that no proof of the aldehydic nature of oxidised cellulose was obtained.

Subsequently Knecht (*Journ Soc Dyers & Col*, 1921, xxxvii 76) discovered that when oxidised cellulose (prepared by the $H_2SO_4 + KMnO_4$ method) was heated with Rosinduline 2B in the presence of caustic soda, its original copper number of 11 was reduced to 0·9, though it still resisted dyeing with this dye-stuff On the other hand, the highly oxidised cellulose was dyed with Primuline, a type of dye which is not affected by reducing agents. In further work it was also found possible to restore the affinity of oxidised cellulose for direct dye-stuffs by boiling it for an extended period with caustic soda or a dyestuff such as Rosinduline In technical practice, mercerisation of cotton fabrics containing oxidised cellulose has for many years been considered as a means of removing this fault.

Oxidised Cellulose and Diazotised Amines.

In a research on the production of pigments by the action of diazotised aromatic amines on tannic acid, Everest and Hall (*Journ Soc Dyers & Col.*, 1921, xxxvii 229) noticed a strong development of colour when oxidised cellulose was treated with a solution containing tetrazotised benzidine. This observation was therefore investigated (*Journ Soc Dyers & Col.*, 1923, xxxviii 47) in order to ascertain whether oxidised cellulose was capable of forming an azo compound.

Samples (0·5 g) of oxidised cellulose, prepared by the permanganate method of Knecht and Thompson, were immersed for 10 minutes in a solution (100 c.c. cooled with ice) containing 1/400 mol of the diazotised amine and 20 c.c. of $N/1$ caustic soda, followed by thorough washing in cold water; the following results were obtained

TABLE XCIV

Amine	Colour of Oxidised Cellulose	Colour produced on Pure Bleached Cellulose.
Aniline	Pale yellow.	Stained slightly yellow
o-Toluidine . . .	Yellow (pinkish)	,, ,,
p-Toluidine . . .	,, ,,	,, ,,
p-Nitraniline . . .	Deep yellow	Pale yellow.
Sulphanilic acid .	Stained slightly yellow.	Colourless.
Benzidine .	Deep brown	Stained pale yellow
Tolidine . . .	Deep reddish brown	,, ,,

It is thus evident that in all these instances the colour produced on the oxidised cellulose is yellow to brown, while pure bleached cellulose is comparatively almost unaffected. The colours produced are quite fast to washing and were scarcely affected when boiled in water. On the other hand, when the coloured cellulose (immediately after being withdrawn from the tetrazotised

11

benzidene solution) is thoroughly washed in cold water and then immersed in
an alkaline solution of naphthol, it quickly suffers a colour change (becoming
reddened), thereby showing the presence of a residue containing a diazotised
amino group.   This would suggest that oxidised cellulose has a strong affinity
for the tetrazotised amine as such.

Quite evident also is the fact that oxidised cellulose is much more reactive
towards diamines of the benzidine type than monamines, the shades developed
by the former being quite deep and fast to washing

Subsequently Everest and Hall investigated the quantitative relations
between oxidised cellulose and tetrazotised benzidine, but no definite evidence
could be found for the existence of an azo compound containing a cellulose
residue   It was, however, shown that the method could be developed for
detecting the comparative degrees of oxidation of cotton fabrics

Comparison of Types of Oxidised Cellulose.

It appears that oxidised cellulose behaves quite differently from pure cotton
towards acids and cellulose solvents   Thus, Hardt-Stremayr has determined
the yield of octoacetylcellobiose (see page 187) from various acetylated oxidised
cellulose under standard conditions   Some of his results are given below

TABLE XCV

Type of Cellulose.	Yield of Octoacetylcellobiose
Cellulose	25 per cent
Hydralcellulose (obtained by action of H_2O_2 on cellulose)	25 ,,
Cellulose oxidised by $KClO_3 + HCl$.	10 ,,
,, ,, HNO_3 . .	16 ,,

It would therefore seem that oxidised cellulose contains fewer cellobiose
groups than ordinary cellulose.

Berl and Klaye (Zeit angew Chem , 1907, xx 381) have ascertained the effect
of oxidation of cotton on its behaviour towards nitrating mixtures (nitric and
sulphuric acids).   They prepared various types of oxidised cellulose by the
following methods ·

1 Cotton wool was treated with boiling 2 per cent sodium carbonate
solution to remove fatty matters and was then thoroughly washed with distilled
water until it had no alkaline reaction.   This pure cotton yielded by analysis :
C=44·38 per cent , H=6·35 per cent.

2 The purified cotton was immersed in 3 per cent. sulphuric acid, squeezed,
dried and heated for 3 hours at 70° C   Analysis C=42·75, H=6·43.

3. 15 g of purified cotton were treated with a 30 per cent. solution of hydrogen peroxide for 30 days   Analysis. C=43·24, H=6·25.

4 32 g of the purified cotton was treated for 36 hours with a solution of 30 g of potassium permanganate dissolved in 300 c c of water, and the product was then decolourised with sulphurous acid and afterwards treated with sulphuric acid.   Subsequently, the product was dissolved in 10 per cent caustic soda and reprecipitated by addition of acid. Analysis C=43·61 per cent , H=6·30 per cent.

5 25 g. of the purified cotton were immersed during one day in 400 c c of water containing 75 g of chalk and 5 g of bromine   The bromine was then driven off by heating the mixture on a water bath and the product further shaken with 5 g of bromine and 75 g of chalk, and afterwards washed   Analysis C=43 83 per cent , H=6·31 per cent.

6 5 g of the purified cotton were immersed for 1 week in 1000 c.c. of water containing 22 g of calcium permanganate, and afterwards decolourised with sulphurous acid.   Analysis C=43 52 per cent , H=5·20 per cent

7 50 g of the purified cotton was heated on a water bath for 2½ hours with 350 c c of nitric acid of sp gr. 1·3   Analysis C=43 17 per cent , H=5·95 per cent.

8. 30 g. of purified cotton was heated at 100° C in 3000 c c. of water containing 150 g of potassium chlorate to which 135 c c. of hydrochloric acid (sp. gr 1·16) was gradually added   Analysis C=43·34 per cent , H=6·39 per cent.

9 Some of the purified cotton was allowed to stand in a solution of bleaching powder (sp gr. 1·07) exposed to air, afterwards washed with slightly acidified water. Subsequently the product was dissolved in 10 per cent. caustic soda and reprecipitated with addition of acid   Analysis C=43·62 per cent , H=6·36 per cent.

These types of cellulose were then examined with the following results ·

TABLE XCVI

Cellulose.	Ash	Absorption of Methylene Blue	Colouration with		Copper Number
			$I+H_2SO_4$	$I+ZnCl_2$	
1 . .	0·10 per cent	3 7	Blue	Blue-violet	7
2 . .	0·18 ,,	4 1	Blue	Blue.	6
3 . .	0·16 ,,	6·5	Blue	Blue.	4
4 . .	0 96 ,,	4·4	Blue	Blue.	7
5 . .	1·20 ,,	6·0	Pale blue	Blue	1
6 . .	0·77 ,,	6 7	Pale brown	Blue.	5
7 . .	0·27 ,,	6·8	Yellowish	Blue.	2
8 . .	0·32 ,,	9 5	Yellow brown.	Blue	1
9 . .	0·55 ,,	8·1	Pale blue	Blue	3

Subsequently these products were nitrated for 24 hours at 20° C with a mixture of acids having the following composition .

Sulphuric acid . .	46 22 per cent
Nitric acid	42·03 ,,
Nitrous acid . .	0·25 ,,
Water . .	11·50 ,,

and then thoroughly washed in water for 3 days   In this manner, a number of nitrated products were obtained and compared thus

TABLE XCVII

Nitrated Product from	N-content.	Solubility in Ether-Alcohol	Methylene Blue Absorption (mg per g)	Relative Viscosity.
1 . .	13·5 per cent	1 8	0·6	10000
2 . .	.	.	..	..
3 . .	13·2 ,,	12·1	2·4	65·7
4 . .	13·3 ,,	18·0	1·6	5·15
5 . .	12·9 ,,	15·5	3·5	9·1
6 . .	13·25 ,,	20·5	3·5	11·1
7 . .	12 9 ,,	34·0	5·0	7·9
8 .	13·9 ,,	18 0	3 0	7·2

From the above results, it is evident that oxidation of cotton greatly increases the solubility in ether-alcohol, the absorption of Methylene Blue, and decreases the viscosity of the resulting nitrated cellulose.   It does not apparently affect the nitrogen content

Oxidised cellulose has also been shown by Schwalbe and Robinoff (*Zeit. angew Chem*, 1911, xxiv 256) to be more susceptible than pure cotton to treatment with water   The degradation of the cellulose in these investigations was measured by the increase in the copper number.   Some overbleached cotton was heated with water under pressure at various temperatures and the results obtained are given below

TABLE XCVIII

Temperature of Treatment	Copper Number of Product
20° C	0·368
100°	0·312
120°	0 331
135°	0 400
150°	0·479
165°	1·43
179°	1.78
213°	3·43

The increase of copper number is thus much more marked when the heating is effected at a temperature exceeding 150° C

Many years ago Weber (*Journ Soc Chem Ind*, 1893, xii. 118) determined the loss in weight suffered by pure scoured cotton when subjected to treatment such as fabric may undergo when dyed under technical conditions. This loss of weight was probably largely produced by oxidation and his results are therefore interesting ; they were obtained with 100 g. of scoured bleached cotton dried at 85° C

TABLE XCXI

Loss of Weight in Presence of

Treatment of 6 hours with Boiling Liquor containing	Oxygen	Steam+ Oxygen	Air	Steam+Air.
5 per cent. NaOH . .	11·05%	17·3%	5·2%	9·2%
5 ,, KOH . .	22·8	29·8	8·4	11·7
5 ,, Na$_2$CO$_3$ . .	8·2	10·1	3·9	5·4
5 ,, K$_2$CO$_3$ . .	13·7	16 4	5·3	6·9
5 ,, Na$_2$B$_4$O$_7$ . .	5 9	6 9	2·2	2 8
5 ,, Na$_2$HPO$_4$. .	3·1	3·5	2·05	2·3

It would therefore appear that oxidation of cotton is more likely to occur in the presence of potassium than sodium alkalis, and as might be expected, more likely in the presence of oxygen than air

Bancroft and Currie (*Journ Phys Chem*, 1915, xix 159) have prepared various types of oxidised cellulose and compared their properties The raw material for these investigations was surgeons' cotton wool which had been boiled for a number of hours with dilute caustic soda and then washed

1. 35 g. of the purified cotton was heated with 350 c c of 60 per cent nitric acid on a water bath for 20 hours The product was filtered through calico, twice washed with 60 per cent nitric acid, and then successively washed with water, 60 per cent alcohol, 90 per cent alcohol and then with ether The material was afterwards dried and ground to a powder, clear white in colour.

2 32 g of the purified cotton were heated with 3000 c c of 15 per cent. sulphuric acid containing 32 g of potassium permanganate on a water bath until the solution was decolourised. This treatment was repeated and the gelatinous product was then freed from manganese by heating it with 15 per cent. sulphuric acid, the product being finally washed with water, 90 per cent alcohol and ether. It was of a light creamy colour

3. 30 g. of the purified cotton was heated to boiling for 1 hour with 3000 c c.

of water containing 150 g of potassium chlorate   From time to time, 125 c c of concentrated hydrochloric acid was added, and the product afterwards washed with water, 90 per cent alcohol and then ether.   The dry product was light and flocculent and composed of short fibres

4   30 g of the purified cotton was digested for 24 hours in 1000 c.c. of a filtered solution of bleaching powder of sp gr 1·03   The treatment was repeated and the product washed with water, 90 per cent alcohol and then with ether   A white flocculent powder was thus obtained

5   30 g of the purified cotton were hung on glass rods in the air and maintained moistened with a similar solution of bleaching powder for 5 days.   In this period, about 700 c c of the bleaching solution were used.   The product was washed with water, 90 per cent alcohol and then with ether, and was found to be similar but slightly more fibrous than that obtained by method 4

The solubilities of these oxidised cottons in caustic potash were determined ·

TABLE C

Type and Amount of Oxidised Cellulose.		Amount of Solvent —10 per cent KOH	Duration of Heating at 100° C	Amount Dissolved
1	1 g	200 c c	24 hours	43·3 per cent
2	1	,,	,,	41 1 ,,
3	1	,,	,,	45·3 ,,
4	1	,,	,,	24 9 ,,
5	1	,,	,,	29 4 ,,

It was concluded that the insoluble portion was really unchanged cotton.

However prepared, oxidised cellulose is stated to have the following properties

1   Does not change colour on heating at 100° C in air

2   Forms a gelatinous mass when warmed with water

3   Partly soluble in caustic soda or potash   In those oxidised cottons prepared, the colour was yellower in caustic potash than in caustic soda

4   Dissolves readily in water after precipitation from alkaline solution with alcohol or acid and dialysis.

5. Dissolves partially when boiled with sodium carbonate solution.   It can then be precipitated with alcohol and is then soluble in water

6. Reduces Fehling's solution if not heated too long previously, for it is found that this reducing property is lost when the oxidised cellulose is heated

7. Not intensely coloured by absorption of copper, aluminium or iron Of these three metals, the iron is absorbed the most strongly and copper least.

8 Charred by action of concentrated sulphuric acid

9 Contains unchanged cellulose in considerable amounts.

These workers further conclude that there is no evidence for the existence of the three different oxidised celluloses a-oxidised cellulose (insoluble in dilute alkali), β-oxidised cellulose (soluble in dilute alkali) and γ-oxidised cellulose (soluble in water), since—(a) a-oxidised cellulose is apparently unchanged cellulose possibly contaminated with decomposition products, and (b) β- and γ-oxidised celluloses are the same substance in different degrees of agglomeration

Detection of Oxidised Cellulose.

The chief characteristics among those described above are low tensile strength, high reducing power, high solubility in caustic alkalis often with the production of a yellow colour, a pronounced affinity for basic dyes and a lack of affinity for direct dyestuffs

The reducing power of oxidised cellulose is usually considered in relation to alkaline solutions of copper hydroxide and is referred to in Chapter V. (see page 136), and the methods for measuring this reduction are described in Chapter X. (see page 216). A pure cotton should have a copper number not exceeding 0·1–0·3, whereas oxidised celluloses having copper numbers of 14 have been prepared and described (see page 137)

Harrison has also devised a method for quickly detecting the reducing power of oxidised cellulose A solution of silver is prepared by adding a solution of silver nitrate to one containing sodium thiosulphate with vigorous agitation, and afterwards adding a solution of caustic soda, such that 100 c c of the final solution contain 1 g of silver nitrate, 4 g of sodium thiosulphate and 4 g of caustic soda When oxidised cotton is boiled in this solution, reduction takes place and the cotton is stained to a depth approximately proportional to this degree of degradation.

Oxidised cellulose may also be shown by Everest and Hall's method (see page 153) In this method, the oxidised cotton should be placed for 10 minutes in 500 c c of an ice-cooled solution containing 1/100 mol of tetrazotised benzidine and 60 c c of N/1 caustic soda Afterwards the cotton should be well washed in cold water and then dried. The depth of brown colour thereby developed on the cotton is a measure of the degree of degradation of that cotton. Mercerised and acid-treated cotton (hydrocellulose) are but slightly stained under the same conditions.

The solubility of oxidised cotton may be determined under any suitable and comparative conditions, caustic soda of 10–18 per cent. being usually employed.

An increased affinity for basic dyes is easily shown by dyeing normal cotton together with oxidised cotton in a 0·05 per cent solution of Methylene Blue. If the cottons are then well washed with water, the oxidised cotton is coloured much more strongly than the normal cotton

CHAPTER VII

CELLULOSE AND DYES

THE dyeing of cotton is probably one of the most important processes connected with the treatment of this fibre, for in modern times there is an increasing desire for highly-coloured articles of clothing and decoration. Coloured materials which were once referred to as being *gaudy* are now spoken of as being in *pleasing contrast*, and the terms *gloomy* and *depressing* are applied to those colours which were formerly thought to be *modest* and *subdued*. This chapter will therefore be devoted to the general principles and methods of dyeing ; technical details may be found in the numerous books already available

The chief methods of colouring cotton are .

1. Immersion of cotton in a solution of a dyestuff having a definite affinity for cotton.
2. Impregnation of cotton with an organic or inorganic substance (mordant) which may or may not have an affinity for the fibre but which serves, when the cotton is subsequently immersed in a solution of a dyestuff, to attract and fix that dye within the cotton.
3. Direct production of a dyestuff within the cotton fibres by ·
   (a) Impregnation of cotton with an organic substance (usually an amine) which is afterwards oxidised *in situ*.
   (b) Formation of insoluble azo colouring matters within the cotton by the usual method of diazotisation and coupling.
4. Immersion of cotton in a solution containing a dyestuff in a reduced soluble form and capable of being absorbed by the cotton. When the cotton is afterwards withdrawn, the absorbed dye is oxidised, either during exposure to the air or by treatment with a solution of an oxidising agent such as a peroxide, to its stable insoluble form, and is thereby fixed within the cotton.

All of these methods are used in technical practice but they yield dyeings of varying fastness. Generally, however, the dyes which are fastest to washing and similar treatment are those which are produced within the cotton fibres in an insoluble form. The affinity of cellulose for direct dyes is so small that cotton dyed by means of them can be progressively stripped by repeated immersion in hot water or dilute solutions of soap.

METHOD I

Dyes available for the first method of dyeing are usually classed together as " direct cotton dyestuffs," or often more simply, " direct dyes." Several

types of compounds, however, are included in this class, and they may be classified thus.

$$
(a) \text{ Azo compounds} \begin{cases} \text{Mono-azo dyes} \\ \text{Disazo dyes} \\ \text{Trisazo dyes.} \\ \text{Tetrakisazo dyes.} \end{cases}
$$

(b) Stilbene compounds
(c) Thiazol compounds
(d) Azine-azo compounds.

Azo Compounds.

The greater number of the direct dyes are azo compounds, and the following are the most important types

Mono-azo Dyes —Not many mono-azo compounds have a direct affinity for cotton, and in those that are known, this affinity is largely due to the presence of special groups. Thus, in Rosanthrene O and Diazo Brilliant Orange GR extra, cotton dyeing power is derived from J-acid

Rosanthrene O
(from J-acid)

Diazo Brilliant Orange GR extra
(from J-acid)
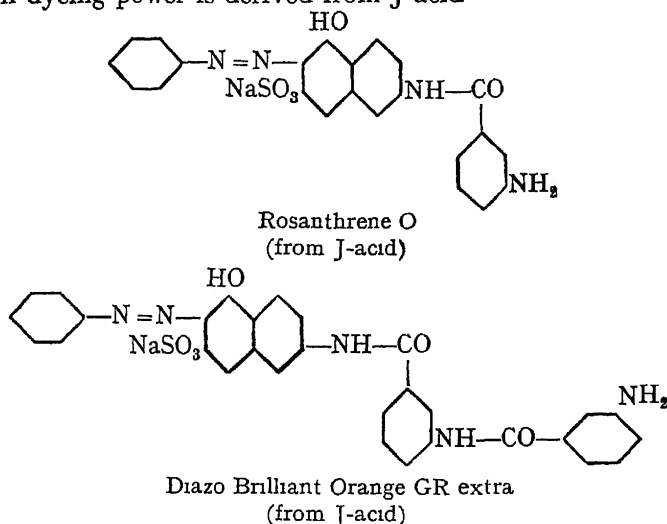
Erika 2GN and Brilliant Geranine 2BN are direct mono-azo dyes, largely deriving their cotton dyeing properties from the presence of thiazol groupings

Erika 2GN
(from de-hydrothio-*p*-toluidine)
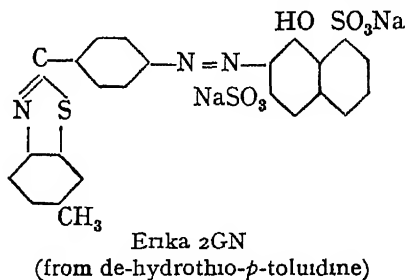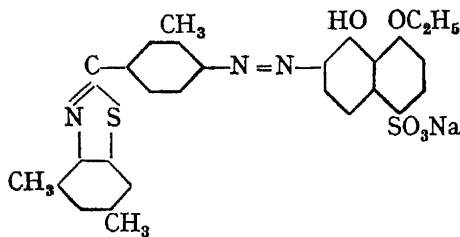
Geranine 2BN
(from de-hydrothio-*m*-xylidine)

In Cotton Yellow R and Chlorophenine Y two thiazol groups are present :
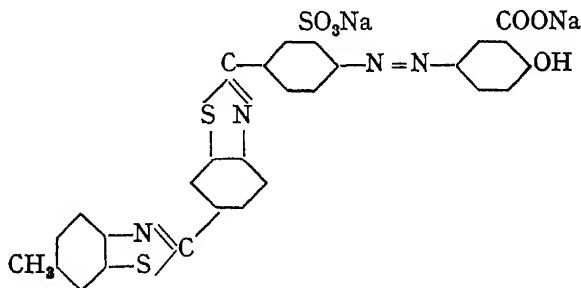
Cotton Yellow R
(from the sulphonic acid of Primuline).
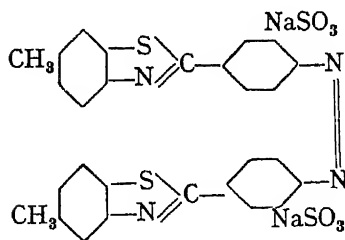
Chlorophenine Y
(from the sulphonic acid of dehydrothio-*p*-toluidine).

Chlorophenine Y is interesting since it is not formed by the usual diazo reaction, but is prepared by oxidation of the ammonium salt of dehydrothio-*p*-toluidine sulphonic acid with sodium hypochlorite.

Disazo Dyes —These, the most important cotton dyes, are obtained from benzidine, tolidine and dianisidine, although cotton has no affinity for these substances as such.

Congo Red was the first azo direct dyestuff discovered (by Bottiger in 1884).

Benzopurpurine 4B soon followed, and though not very fast to acids is still largely used.   Chlorazol Sky Blue FF is one of the best cotton blues available.
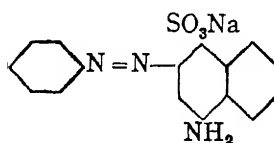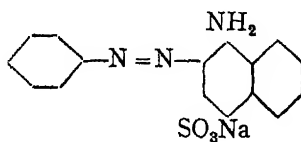
Congo Red
(from benzidine)
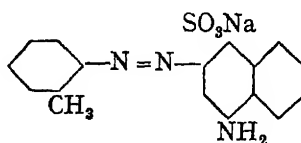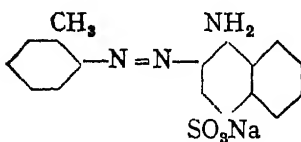
Benzopurpurine 4B
(from tolidine).
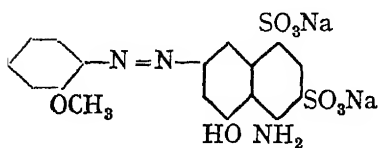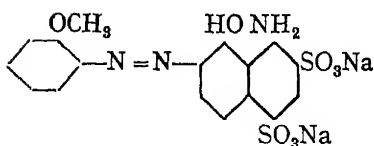
Chlorazol Sky Blue FF
(from dianisidine)

Direct dyes are also obtained from benzidine sulphone and diamino-carbazol :
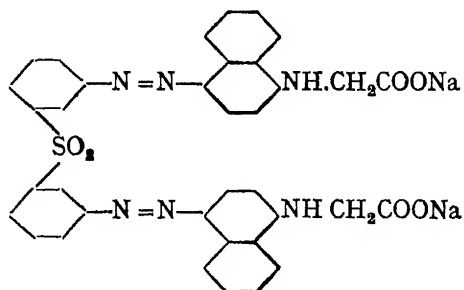
Glycine Blue
(from benzidine sulphone)
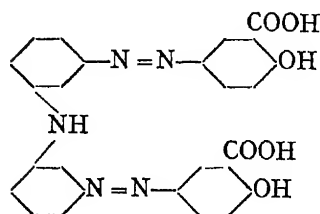
Carbazol Yellow
(from diamino-carbazol).

Similarly, disazo cotton dyes are obtained from *p*-phenylene diamine (not *m*-phenylene diamine), diaminodiphenylamine (see page 176), diaminoditoly-lamine, 1·5-diaminonaphthalene and 1·4-diaminonaphthalene
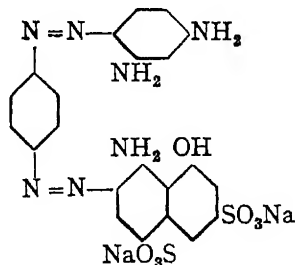
Para Black R
(from *p*-phenylene diamine)

CH₃   NH₂

—N =N—   NH₂
              CH₃

NH

          HO
—N =N—   NH₂
CH₃   NaSO₃
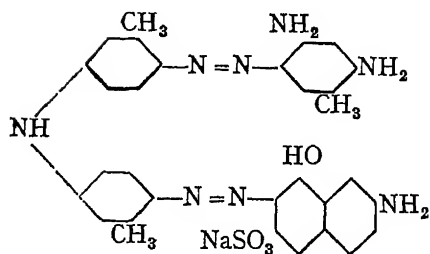
Diphenyl Fast Black
(from diamino-ditolylamine)

N =N—   OC₂H₅

NaSO₃
      NaSO₃

C₂H₅O   —N =N
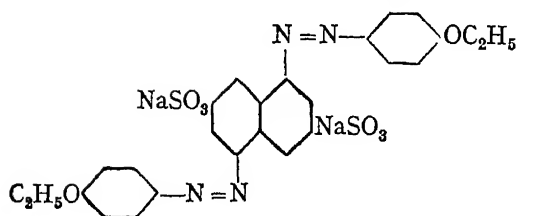
Diamine Gold
(from 1 5-diaminonaphthalene)

N =N—   NH₂

NaSO₃
      NaSO₃

NH₂   —N =N
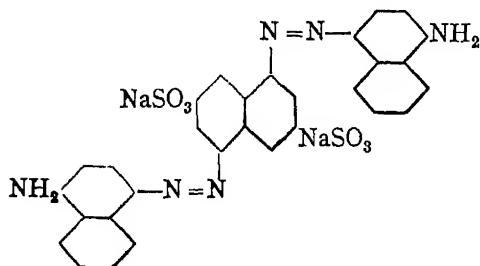
Naphthylene Violet
(from 1 4-diaminonaphthalene)

Certain urea compounds such as diamino-diphenylurea and diamino-diphenylthiourea, yield disazo dyes capable of dyeing cotton thus .

          NaSO₃
      NaSO₃   HO
NH—   —N =N—
                  NH₂
CO

              NH₂
NH—   —N =N—
      NaSO₃   HO
                  NaSO₃
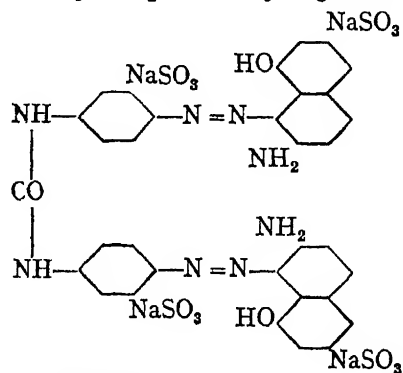
Chlorazol Fast Pink BK
(from diamino-diphenyluera)
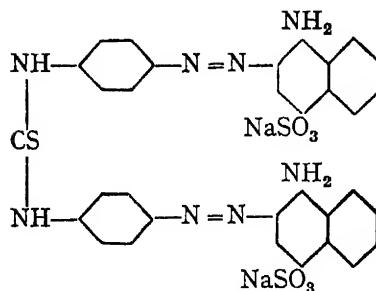
Salmon Red
(from diamino-diphenylthiourea).

Disazo compounds derived from p-diamino-diphenylmethane and p-diamino-dibenzyl have no affinity for cotton. On the other hand, disazo derivatives of diamino-stilbene are direct dyes
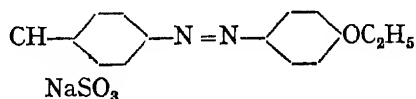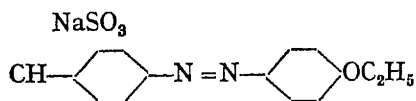
Chrysophenine G
(from diaminostilbene disulphonic acid).

St Denis Red is a curious disazo cotton dye prepared from diamino-azoxytoluene ·
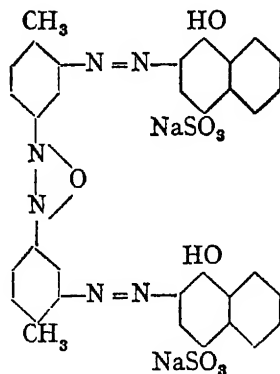
St Denis Red
(from diaminozaoxytoluene).

Trisazo Dyes.

These dyestuffs are prepared from various amines and usually have a tertiary colour. The following are typical:

Columbia Black FF

Chlorazol Dark Green PL.

Chlorazol Brown G

Chloramine Blue 3G
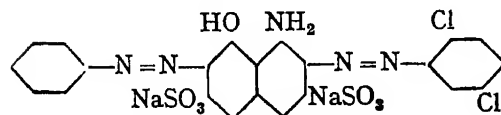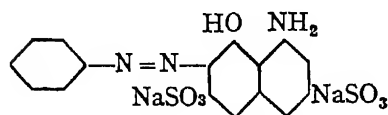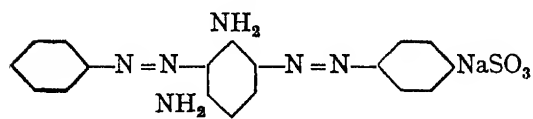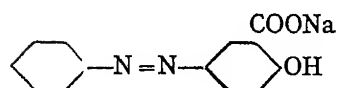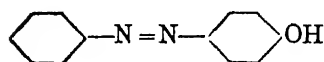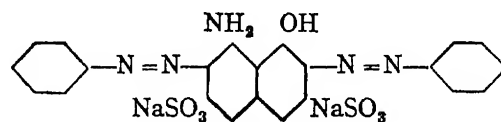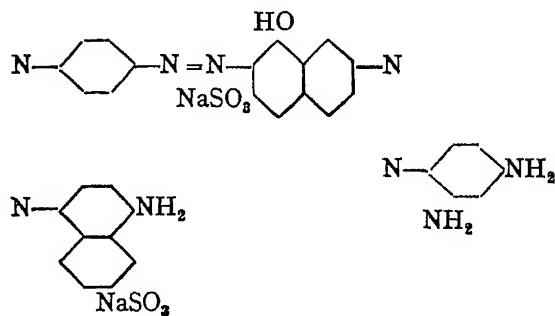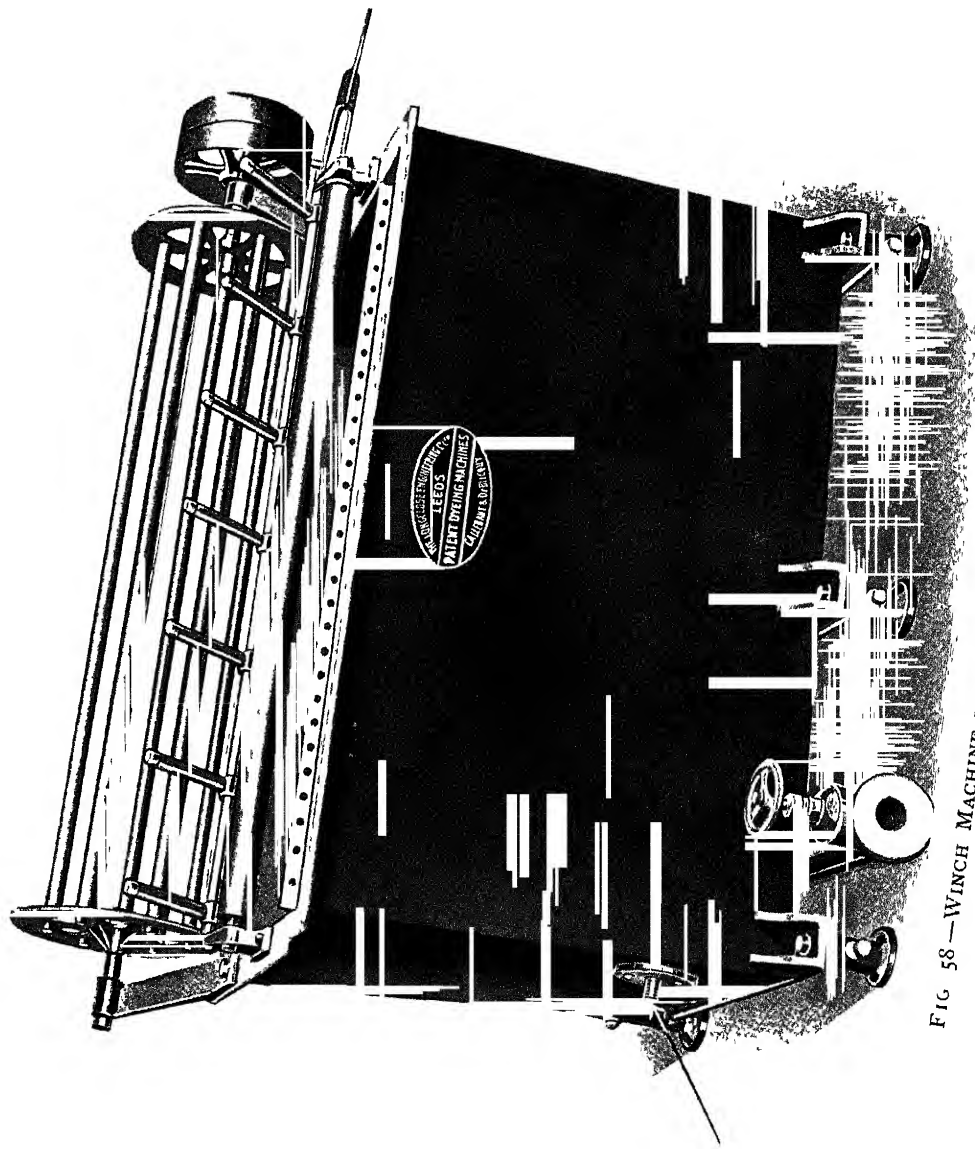
FIG. 58—WINCH MACHINE FOR DYEING KNITTED COTTON MATERIALS

(The Longclose Engineering Co Ltd)
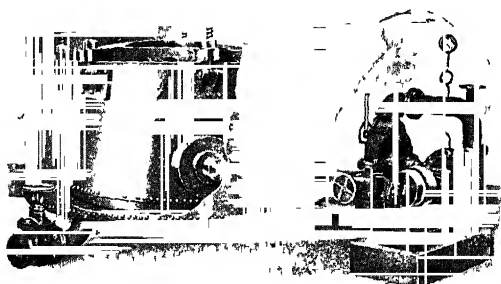
FIG. 591.—MACHINE FOR DYEING LOOSE COTTON
(The Longclose Engineering Co. Ltd.)

TO RESERVE
TANK
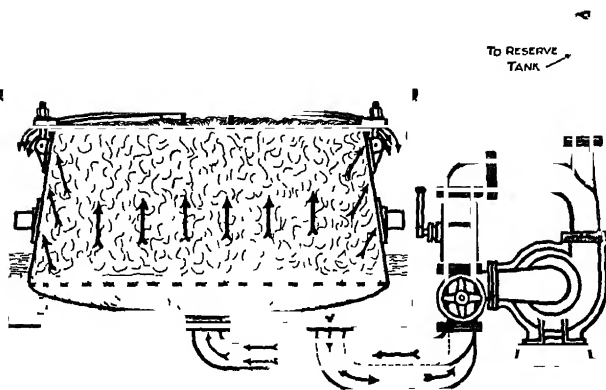
FIG. 591.—SECTIONAL VIEW OF MACHINE FOR DYEING
LOOSE COTTON
(The Longclose Engineering Co. Ltd.)
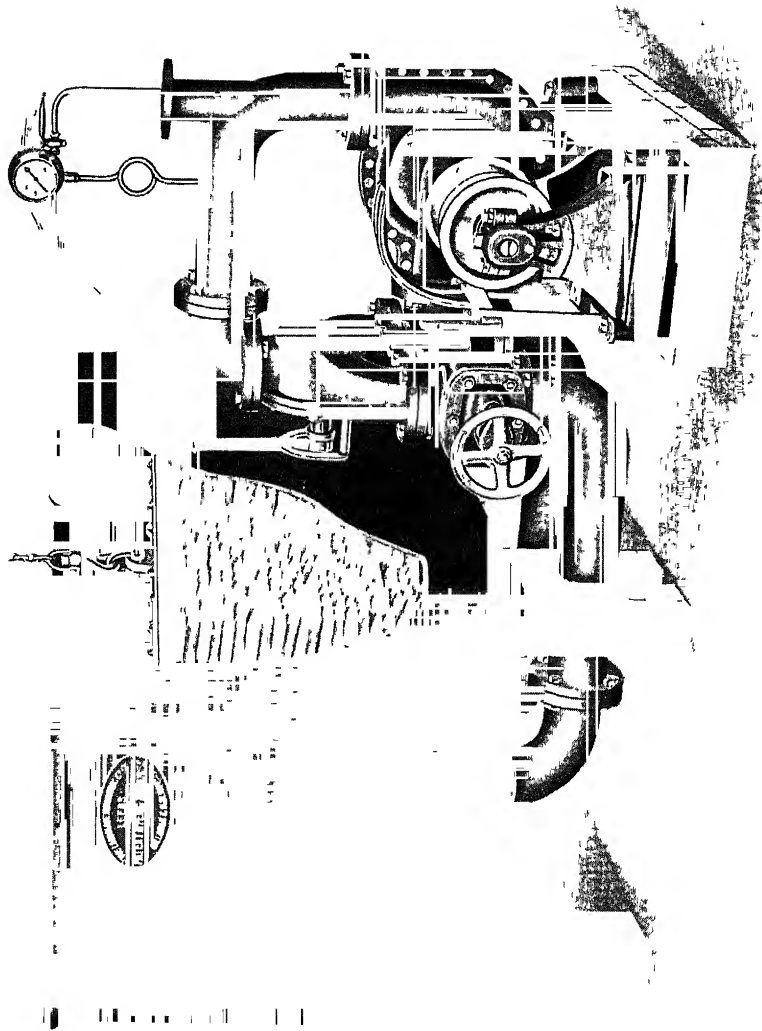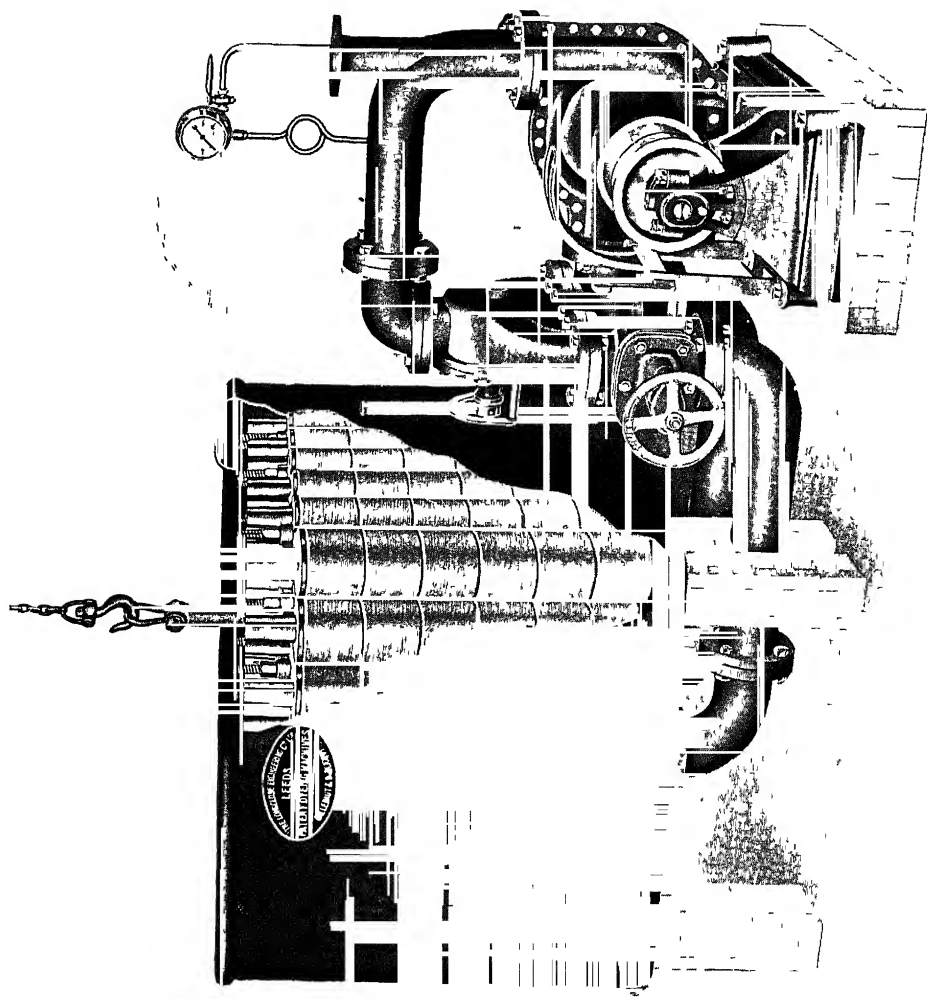
FIG. 60A — MACHINE FOR DYEING COTTON YARN IN COPS
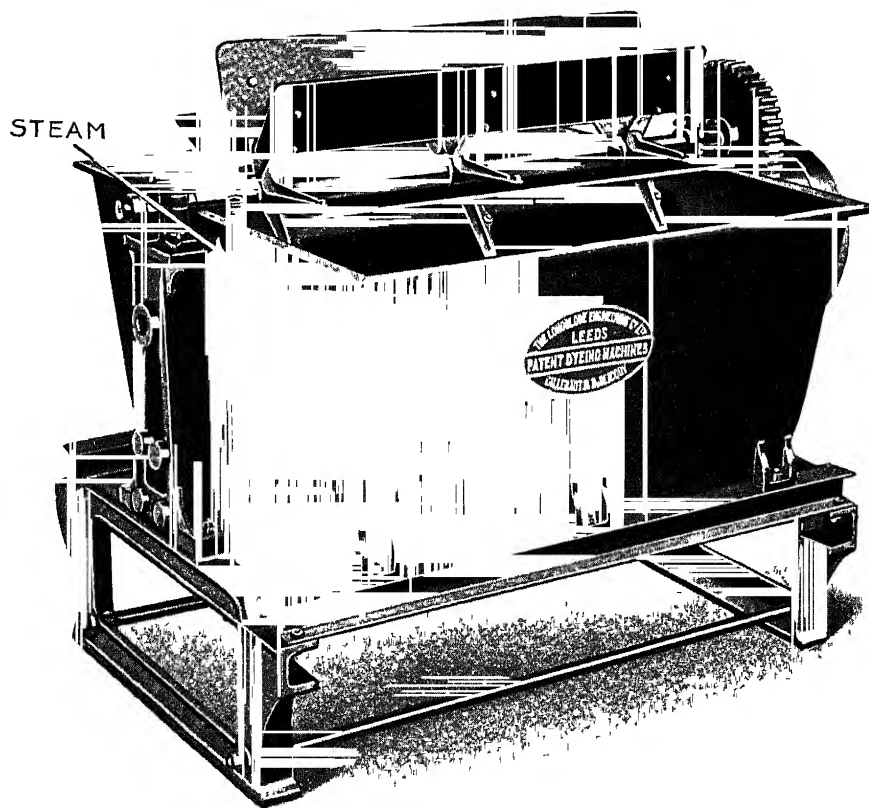
(The Longclose Engineering Co Ltd)
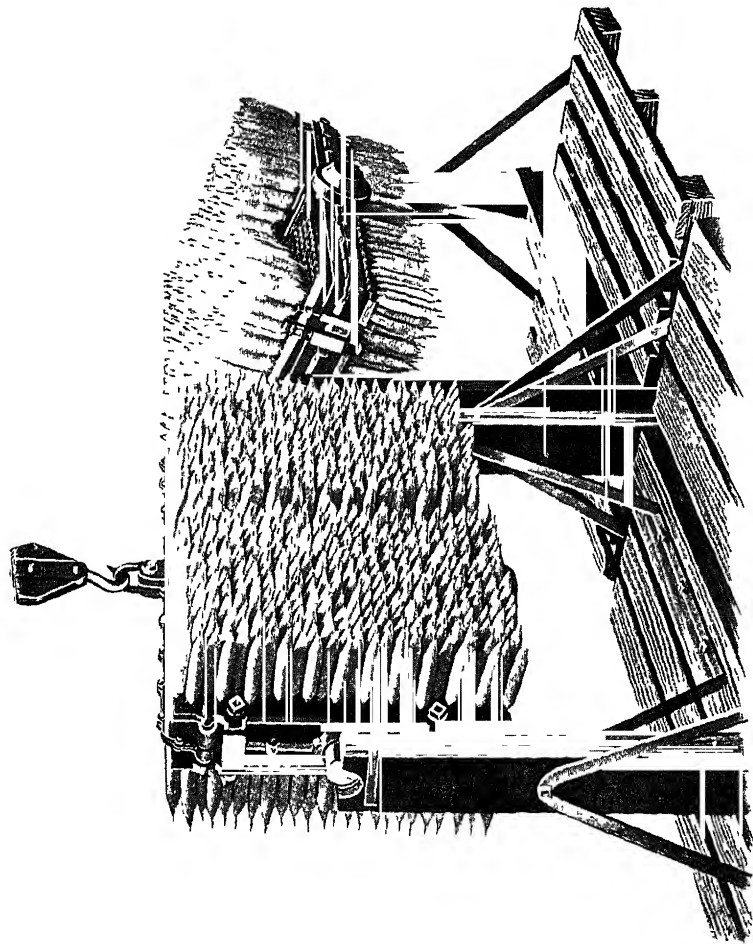
FIG 60B.—FRAME OF COTTON YARN COPS BEFORE BEING PLACED IN A
COP DYEING MACHINE (FIG 60A)

(The Longclose Engineering Co Ltd)

Tetrakisazo Dyes.

These cotton dyes are usually brown or black, and the following are examples:

NH₂ groups structure — Naphthamine Fast Black.

Naphthamine Fast Black.

structure

structure — Cotton Brown A.

Cotton Brown A.
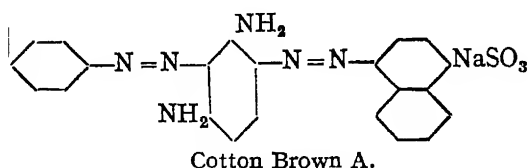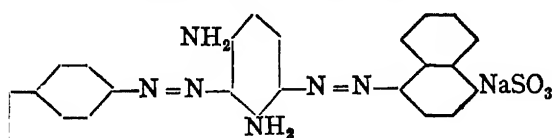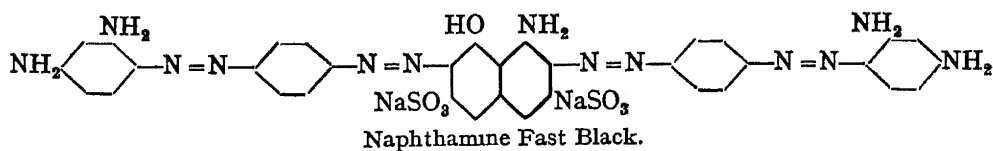
It is often possible to colour cotton indirectly by means of trisazo and tetra-kisazo compounds   Thus, when cotton is dyed with an azo compound containing a free amino group, the dyed cotton may be treated afterwards with nitrous acid and then with a developer such as β-naphthol, resorcinol or β-hydroxynaphthoic acid, whereby further coupling takes place and deeper and faster shades are produced   This process is frequently employed for the production of deep fast blacks and browns, such dyes as Chlorazol Black BH and Chlorazol Brown M being treated in this manner

An alternative method for obtaining similar results consists of treating cotton dyed with a suitable dyestuff, with a solution containing a diazotised amine such as paranitraniline, under conditions such that coupling occurs. Chlorazol Black BXX and Chlorazol Brown GM may be treated in this manner.

Stilbene Compounds.

A limited number of direct dyes are of the Stilbene type, and they are mainly produced from p-nitro-toluene-o-sulphonic acid   The following dyes are typical ·

structure — Stilbene Orange G.

Stilbene Orange G.

12

$$NaSO_3 \qquad\qquad NaSO_3$$

$$CH\langle\bigcirc\rangle\text{—N}=\text{N—}\langle\bigcirc\rangle CH$$

$$CH\langle\bigcirc\rangle NO_2 \quad NO_2\langle\bigcirc\rangle CH$$

$$NaSO_3 \qquad\qquad NaSO_3$$

<div align="center">Chlorantine Yellow GG</div>
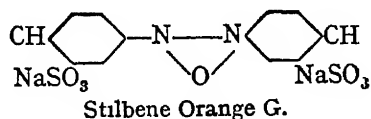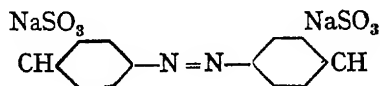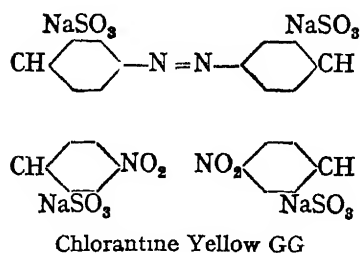
Thiazol Compounds.

These colours were discovered by Green in 1887, when he found that Primuline was formed by heating a mixture of sulphur and p-toluidine at about 200° C Such dyes are very interesting, but of comparatively small importance ; they are not generally fast to light.

Primuline is a yellow cotton dye, but the dyed material may be further diazotised and developed, whereby the following shades can be obtained :

Developer.	Shade.
Phenol.	Yellow.
Resorcinol	Orange.
m-phenylene diamine .	Reddish brown.
a-naphthol . . .	Maroon.
β-naphthol . .	Red.
Aminocarbazol . . .	Brown (fast to light)
a-naphthol 3·8-disulphonic acid .	Maroon.
Naphthol AS	Bordeaux.

Primuline—the commercial dyestuff—consists of a mixture of the following compounds, (a) being present in the largest proportion.

<div align="center">(a)   (b)</div>
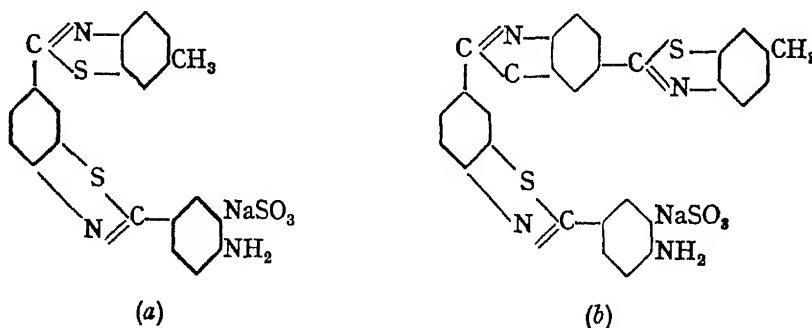
Azine-azo Compounds.

These compounds are produced by coupling diazotised Safranine with various intermediates such as phenol and dimethylaniline. Such dyes are known as
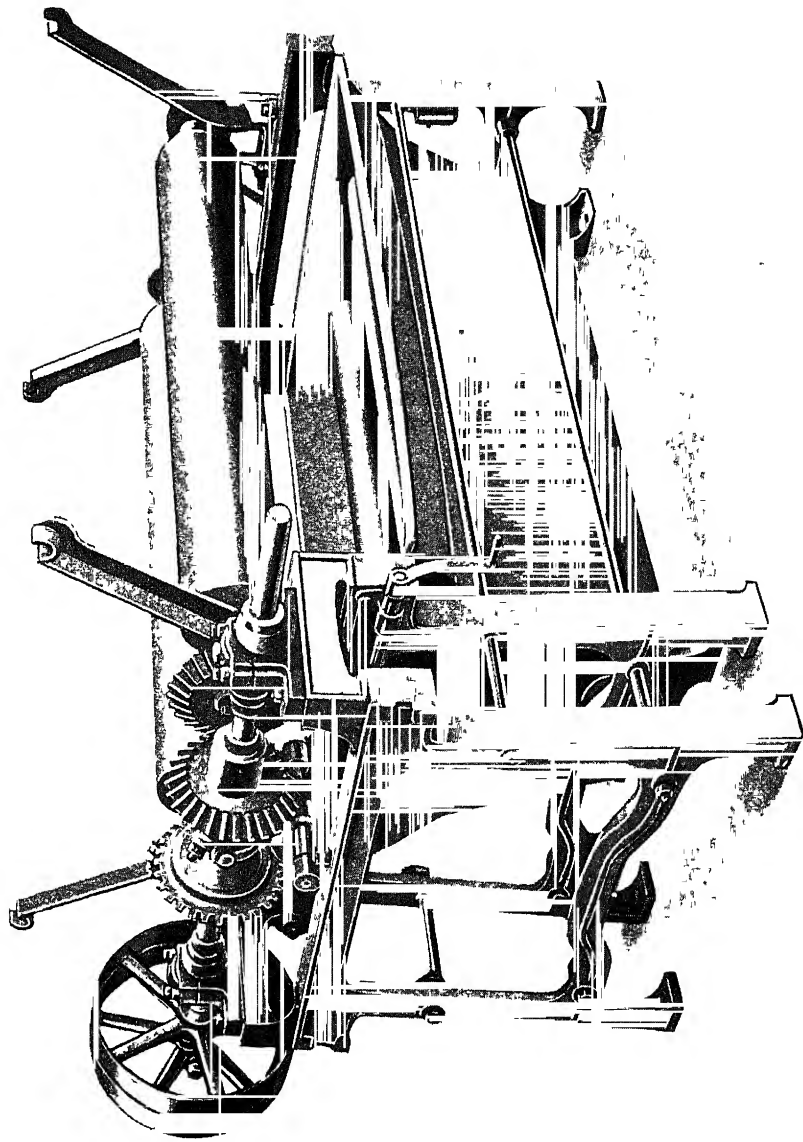
Fig. 61.—Modern Jig for Dyeing Cotton Piece Goods

The Jig surfaces are covered with Haidite, which is waterproof, resistant to acids and alkalis, perfectly smooth and not stained by dyes

(The Longclose Engineering Co Ltd)

FIG. 62.—MACHINE FOR DYEING COTTON YARN IN CHEESES

(The Longclose Engineering Co. Ltd.)

STEAM

Fig 63.—Paddle Machine for Dyeing Cotton Hose, Garments, etc
(The Longclose Engineering Co Ltd)

Janus dyestuffs and possess but only a moderate affinity for cotton ; they are faster on this fibre when fixed with a mordant such as tannic acid. They also have a basic nature which gives them an affinity for wool, so that they are used in union dyeing.
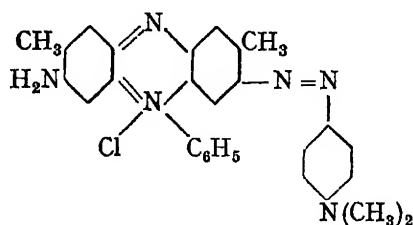
Janus Green G
(from saframine).
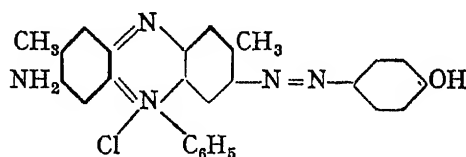
Janus Black
(from saframine)

The application of direct dyes to cotton is a comparatively simple operation, the cotton material being merely immersed in a hot aqueous solution of the dye until the desired shade is obtained. In the case of loose cotton, the dye liquor is usually continuously forced through the cotton in special machines so as to obtain uniformity of dyeing (see Figs. 59A and 59B). Yarns are generally dyed on beams or cops or cheeses (see Figs 60A, 60B, 62), the dye liquor being forced in either direction through the layers of yarn, or alternatively ; the yarn is dyed in skein form (see Figs. 64A and 64B), in which case it is usual to maintain the yarn in relative motion to a more or less stationary dye liquor ; fabrics are usually passed backwards and forwards through a stationary dye liquor contained in a jig (see Fig. 61) or winch machine (see Fig 58). Loose materials and garments are frequently dyed in a paddle machine (Fig. 63).

A large number of direct dyes have their greatest affinity for cotton at about 80° C., and at higher or lower temperatures weaker shades are obtained. Moreover, this affinity affects the degree of exhaustion of the dye liquor. The greater the affinity the better the exhaustion of the dye liquor and the more economical the process of dyeing. It is also found that the addition of certain assistants to the dye liquor is necessary for the establishment of its better control. Such additions may be to hasten or retard dyeing Thus addition of sodium chloride or sodium sulphate has the effect of promoting better exhaustion of the dye liquor and the production of deeper shades , whereas addition of an alkali such as sodium carbonate, caustic soda or soap retards and may almost prevent dyeing.
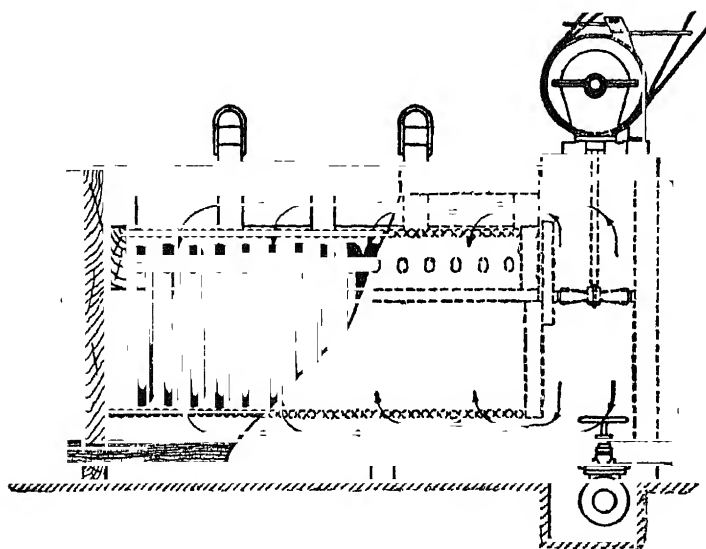
FIG. 64A.—MACHINE FOR DYEING COTTON HANKS.

(The Longclose Engineering Co. Ltd)
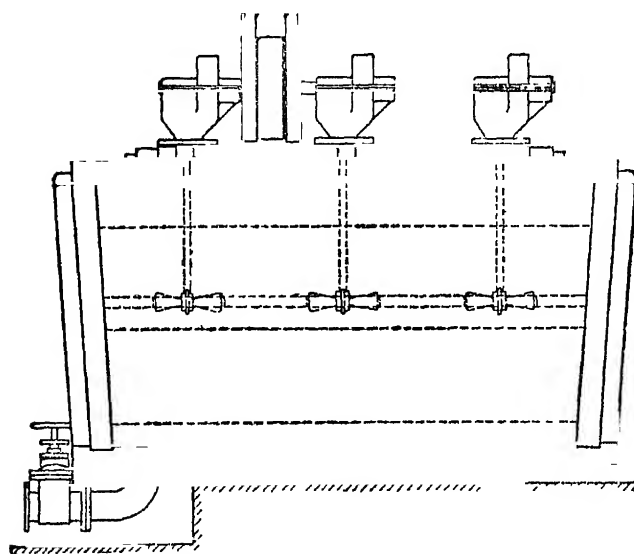
FIG. 64B.—END VIEW OF MACHINE FOR DYEING
COTTON HANKS

(The Longclose Engineering Co. Ltd)

In a recent paper, Bartunek (*Cellulosechemie*, 1924, v. 33) finds that during dyeing in the cold, 25 parts of sodium carbonate or 58 parts of sodium chloride, and in hot dyeing, 41 parts of sodium carbonate and 65 parts of sodium chloride have the same exhausting effect as 100 parts of Glauber's salts. He also observes that sodium carbonate does not exert a retarding effect unless present in a concentration greater than 4 g. per litre.

METHOD 2

In the second method for colouring cotton, the material is first mordanted with a mineral or organic substance and is then immersed in a solution of a colouring matter. Less frequently, this order of operations is reversed.

Cotton has very little affinity for mineral substances, so that the fixation of these in the fibres is usually accomplished by methods of precipitation Thus, cotton is impregnated with a solution of a metallic salt, then partly or wholly dried and immersed in a solution containing a base or other compound which will immediately produce an insoluble compound of the metal, which is thereby fixed within the cotton. This process is adopted for dyeing cotton materials with fast mineral pigments such as iron oxide, Prussian Blue and manganese oxide, but only in the instance of Turkey red dyeing is cotton mordanted with mineral substances for purposes of dyeing; much more frequently is cotton mordanted with tannic acid (see page 100) or its substitutes (katanol). After mordanting with tannic acid, cotton is usually treated with a solution of an antimony salt such as antimony fluoride or tartar emetic, since it has been found that this treatment further fixes the tannic acid and renders the resulting dyeings faster and brighter.

The mordanting of cotton with mineral substances is more largely carried out in printing than in dyeing

After mordanting with tannin-tartar, cotton is dyed by simply immersing it in an aqueous solution of a basic dyestuff, usually cold or heated not above 50° C. Such dyes are drawn from the following classes of compounds

> Di- and triphenylmethane compounds.
> Xanthene compounds.
> Acridine compounds
> Azine compounds
> Oxazine compounds.
> Thiazine compounds
>
> Azo compounds $\begin{cases} \text{Monoazo dyes.} \\ \text{Disazo dyes} \\ \text{Trisazo dyes.} \end{cases}$

The following dyestuffs are given as types of compounds having a basic character which renders them to be applicable to cotton suitably mordanted with tannin-tartar or Katanol.
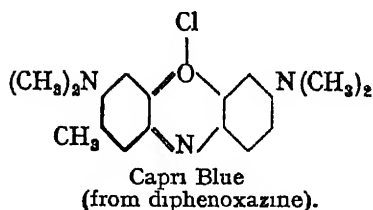
Di- and Tri-phenylmethane Dyes.

C=HN $\quad$ N(CH₃)₂

N(CH₃)₂

Auramıne
(from diphenylmethane)

C——— N(CH₃)₂

=N(CH₃)Cl

Malachıte Green
(from trıphenylmethane)

Xanthene Dyes.

These include the Rhodamınes, which are largely used for the production of brıght bluish red fluorescent shades, but whıch have relatively poor fastness.
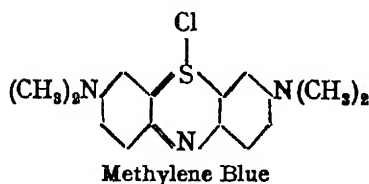
Cl

(C₂H₅)₂N $\quad$ O $\quad$ N(C₂H₅)

C

COOC₂H₅

Rhodamıne 6G
(from phenylxanthene).

Acridine Compounds.

These are also fluorescent.

H $\quad$ Cl

NH₂ $\quad$ N $\quad$ NH₂

CH₃ $\quad$ CH $\quad$ CH₃

Acrıdıne Yellow GR
(from acrıdıne).

Azine Compounds.

Safranine
(from diphenazine).

Oxazine Compounds.

Capri Blue
(from diphenoxazine).

Thiazine Compounds.

Of these, Methylene Blue is one of the best known and most useful.

Methylene Blue

Azo Compounds.

Not many azo basic dyestuffs are employed for cotton, and they have not the same brilliance as shown by basic dyes of other types. Mono-, di- and tri-azo dyestuffs are available

Chrysoidine
(monoazo).

Bismarck Brown
(disazo).

$$Cl(CH_3)_3N$$

Janus Brown B
(trisazo).

The colouring of cotton containing a mineral mordant is almost confined to textile printing. Aluminium and chromium (frequently associated with sulphonated oils) are the most important mineral mordants Alizarin and other similar compounds derived from anthraquinone are the dyestuffs most frequently employed.

Alizarin
(from anthraquinone).

METHOD 3

As previously indicated, the fastest colours are usually produced on cotton by the third (and fourth) method of dyeing. This method may be further subdivided according as the pigment dyestuff is produced by oxidation or processes of diazotisation and coupling

In the oxidation process, which is largely employed for Aniline Black, cotton is impregnated with a solution containing an amine (aniline or aminodiphenylamine for Aniline Black; p-phenylene diamine for Paramine Brown ; m-aminophenol for Fuscamine Brown), an acid (hydrochloric acid), an oxidising agent (sodium chlorate) and a catalyst such as copper sulphate, vanadium chloride or a ferro- or ferri-cyanide. The cotton is afterwards partly or wholly dried and then heated in a moist atmosphere at 50°–105° C., whereby the oxidation occurs and the amine is converted into the desired pigment Usually the oxidation is not quite completed in these processes, so that the cotton is afterwards further oxidised by immersion in a warm or hot solution containing an oxidising agent such as sodium bichromate. It is then merely necessary to remove excess of reagents and by-products from the cotton by washing it in hot water which may or may not contain detergents such as soap.

It has been stated that one-half of the world's production of aniline is

employed for the production of oxidised Aniline Black—a shade which is of extraordinary good fastness to all influences.

The production of insoluble azo compounds within cotton fibres was first carried out by Holliday in 1880, and since then the method has been largely used for dyeing Para-red upon cotton. The procedure, which is common for the production of various shades, consists of impregnating cotton with an alkaline solution of β-naphthol, drying it and then passing it through a solution containing a diazotised amine, whereby development of the colour takes place. Afterwards, the cotton is thoroughly cleansed from adhering impurities by soaping.

β-Naphthol was practically the only naphthol used, but various amines (particularly paranitraniline and α-naphthylamine) are and have been used, the following shades being obtained

Paranitraniline	.	.	.	PARA-RED
α-Naphthylamine				NAPHTHYLAMINE CLARET.
β-Naphthylamine		.	.	Blue red
Metanitraniline		.	.	Orange.
Nitro-toluidine	.	.	.	Orange.
Benzidine	.	.	.	Puce
Tolidine	.		.	Puce
Nitrophenetidine	.		.	Pink
Dianisidine	.	.	.	DIANISIDINE BLUE

In recent years, the method has been made much more important by the investigations of the Chemische Fabrik Greisheim Elektron. As a result, a greater range of fast shades may now be obtained by means of β-hydroxynaphthoic acid anilide substitutes for β-naphthol (Naphthol AS, Naphthol AS-BO, Naphthol AS-RL and Naphthol AS-BS, etc) and various amines. These dyes are in many instances equal in fastness to vat dyes

METHOD 4

The fourth method of dyeing includes the so-called Sulphur and Vat dye-stuffs.

Sulphur Dyes.

These dyestuffs, the first of which was discovered by Croissant and Breton-niere in 1873 but more definitely by Vidal in 1893, are prepared by heating various aromatic compounds with sulphur. They are insoluble except in aqueous solutions containing certain reducing agents such as sodium sulphide or sodium hydrosulphite Their application to cotton is therefore almost universally carried out by immersing the cotton in a sodium sulphide solution of the dyestuff, whereby the reduced form of the dye is absorbed by the cotton. Afterwards,

Janus Brown B
(trisazo)

The colouring of cotton containing a mineral mordant is almost confined to textile printing. Aluminium and chromium (frequently associated with sulphonated oils) are the most important mineral mordants. Alizarin and other similar compounds derived from anthraquinone are the dyestuffs most frequently employed

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Benzidine	.	.	Puce
Tolidine	.	.	Puce
Nitrophenetidine	.		Pink
Dianisidine	.	.	DIANISIDINE BLUE

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the cotton is exposed to the air or to chemical oxidation, whereby the reduced dye is oxidised to its permanent insoluble form within the fibres

Vat Dyes.

Vat dyes, mainly derived from anthraquinone but also from compounds having an indigoid structure, are also inert and only rendered soluble by reduction, particularly by sodium hydrosulphite   Hence these dyes are applied to cotton by a method similar to that used for sulphur dyes, except that hydrosulphite is used instead of sodium sulphide.

The colours obtained by means of sulphur and vat dyes are particularly fast, the latter more than the former.

Theories of Dyeing.

As yet, no satisfactory theory capable of explaining all the dyeing properties of cotton has been suggested.   On the whole, cotton shows itself to be inert towards dyestuffs, and it appears unlikely that any theory involving chemical combination of the dye with cotton could apply to more than a limited number of instances.   Electrical theories have not met with much success, although Harrison (*Journ. Soc. Dyers & Col*, 1911, xxvii. 279) has shown that an electrical potential is developed when cotton is immersed in a dye solution.   It therefore seems likely that a clear understanding of the process of dyeing can only be obtained by investigations in which cotton is considered as a colloid and the dye solution as containing particles of dye whose disperse state may be considerably varied by change of temperature or the addition of electrolytes.

At the present time, considerable research is being carried out by Auerbach and others (*Kolloid Zeit*) along these lines, but it is yet too early to draw any comprehensive conclusions

Thus far, the dyeing of normal cotton only has been considered, but it is evident that degraded or modified cellulose will have different dyeing properties. Thus, cotton tendered by oxidation (see page 160) or by treatment with acids (see page 108) has a pronounced affinity for basic dyestuffs such as Methylene Blue.   Mercerised cotton (see page 74) and viscose and cuprammonium artificial silks (see page 193) have a generally increased affinity for all dyestuffs.   The dyeing properties of cotton are also influenced by its origin and growth.

Birtwell, Clibbens and Ridge (*Journ Text. Inst*, 1923, xiv. 297) have thus found that Egyptian and American cottons can be easily distinguished by their affinity for Methylene Blue.   These types of cotton, after a similar bleaching treatment which included a caustic soda boil under pressure, treatment with a hypochlorite and afterwards with an acid, showed the absorptions of dye as given in Table CI.

Egyptian cotton thus absorbs about twice as much Methylene Blue as does American cotton.

TABLE CI

Samples of American Cotton.	Millimoles of Methylene Blue absorbed per 100 g. of Dry Cotton.
No. 1	0·45
,, 2	0·45
,, 3	0·44
,, 4	0·52
,, 6	0·60
,, 6 . . .	0·46
,, 7	0·43

Samples of Egyptian Cotton.	
No. 1 (Sakellaridis) . .	0·92
,, 2 ,, . .	0·77
,, 3 ,, . .	0·67
,, 4 ,, . .	0·65
,, 5 (Uppers) . .	0·68
,, 6 ,, . .	0·69
,, 7 ,, . . .	0·64

Huebner (*Journ. Soc. Dyers & Col.*, 1921, xxxvii. 139) has also observed that the degree of disintegration of cotton considerably affects its absorption of the basic dye Night Blue. Thus, carefully purified cotton yarn was beaten (as in paper manufacture) for varying periods, and the affinity of the product for Night Blue was then shown to be greater as the time of beating was increased, that is, as the disintegration was more thorough. The following results were obtained ·

TABLE CII

	Time of Immersion in Dye Solution in Hours.	Duration of Beating in Hours.				
		0	1·5	3·0	4·5	6·0
Average length of fibre in mm.	..	23 0	2·5	1·5	1·1	0·7
Per cent. of Night Blue absorbed.	1	14·5	52·2	56·9	58·4	62·3
	6	24·5	58 9	59·2	59·2	62·3
	18	27 6	59·2	59·2	60·1	62·3
	72	32·2	60·7	63·5	64·7	65·3

It was also observed that although the highly disintegrated cotton absorbed twice as much dye as the untreated yarn, the shades of both were equal. This fact is probably connected with the greater amount of surface of the disintegrated yarn.

In technical practice, it is commonly observed that so-called dead cotton has but little affinity for direct cotton dyestuffs, and this property is retained even after mercerisation. Clegg and Harland (*Journ. Text. Inst.*, 1923, xiv. 125) have made some observations bearing on this in an investigation of neps in dyed or printed cotton fabrics These workers suggest that such cotton is really dyed but appears not to be so, for optical reasons ; but further evidence would appear to be required to make this statement more convincing.

CHAPTER VIII

THE CONSTITUTION OF CELLULOSE

FROM the earliest times, cellulose obtained by purification of cotton under conditions which are likely to produce the minimum of chemical change has been known to have the following composition ·

Carbon	.	.	.	44·4 per cent
Hydrogen	.	.	.	6·2 ,,
Oxygen	.	.	.	49·4 ,,

and the simplest formula expressing this fact is $C_6H_{10}O_5$ In view, however, of the comparative inertness of cellulose to almost all reagents, its obvious colloidal nature, and its relationship to starch and other carbohydrates, the molecule of cellulose is most probably more complex and is therefore usually shown as $(C_6H_{10}O_5)_n$.   The problem of all cellulose chemists has therefore been to determine the arrangement of the constituent atoms within the simplest molecule and also the value of n

Recently, the most probable chemical constitution of cellulose has been determined, so that it will suffice briefly to review older theories together with some of the facts on which they were based and then indicate the observations which support the most modern structural formula.

The first formula suggested by Cross and Bevan was ·

$$
\begin{array}{c}
\text{CHOH---CHOH} \\
\diagup \qquad\qquad \diagdown \\
\text{OC} \qquad\qquad\qquad \text{CH}_2 \\
\diagdown \qquad\qquad \diagup \\
\text{CHOH---CHOH}
\end{array}
$$
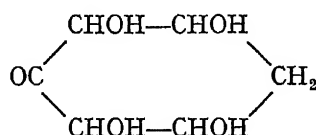
and it was based, among other facts, on the fact that the formation of tetra-acetyl cellulose was possible   It also supported their opinion (*Researches on Cellulose*, i. p. 38) that acetates containing more than four acetyl groups were possible.   The above formula could account for these and explains how in a simple manner (condensation) complex cellulose may be built up thus .

$$
2\ \begin{array}{c}
\text{CHOH---CHOH} \\
\diagup \qquad\qquad \diagdown \\
\text{OC} \qquad\qquad\qquad \text{CH}_2 \\
\diagdown \qquad\qquad \diagup \\
\text{CHOH---CHOH}
\end{array}
\ \longrightarrow\
\begin{array}{c}
\text{CH} \\
\|\| \\
(\text{CHOH})_4 \\
\|\| \\
\text{C.OH}
\end{array}
\qquad
\begin{array}{c}
\text{C OH} \\
\|\| \\
(\text{CHOH})_4 \\
\|\| \\
\text{CH}
\end{array}
$$

or

$$
2\ \begin{array}{c}
\text{CHOH---CHOH} \\
\diagup \qquad \diagdown \\
\text{OC} \qquad\quad \text{CH}_2 \\
\diagdown \qquad \diagup \\
\text{CHOH---CHOH}
\end{array}
\rightarrow\
\begin{array}{c}
\text{CHOH---CH} \\
\diagup \qquad \diagdown \\
\text{OC} \qquad\quad \text{CH}_2 \\
\diagdown \qquad \diagup \\
\text{CHOH---CHOH}
\end{array}
\ \begin{array}{c}
\text{O} \\
\diagdown\ \diagup \\
\text{C} \\
\diagup\ \diagdown \\
\text{HO}
\end{array}
\ \begin{array}{c}
\text{CHOH---CHOH} \\
\diagup \qquad \diagdown \\
\qquad\qquad \text{CH}_2 \\
\diagup \\
\text{CHOH---CHOH}
\end{array}
$$
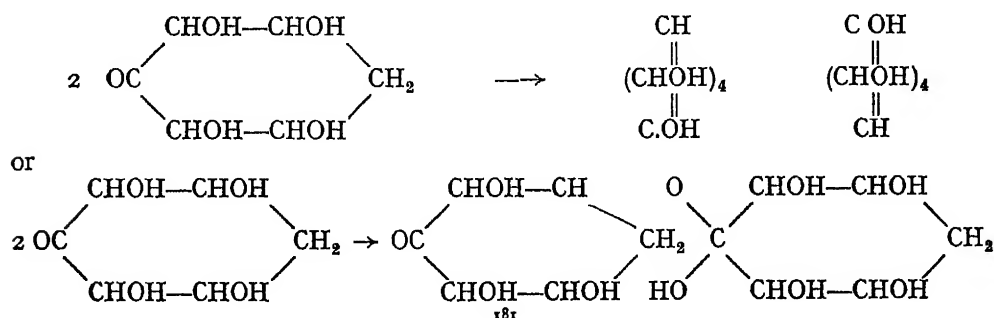
Such a formula would also account for the production of oxalic, tartaric and also other aliphatic acids of low molecular weight and for the non-production of saccharic acid when cellulose was oxidised with nitric acid. It would also account for the production of dihydroxybutyric and iso-saccharic acids when oxycellulose is heated with lime water, and of w-bromomethyl furfuraldehyde when cellulose is treated with hydrobromic acid in the presence of chloroform as described by Fenton and Gostling (*Journ. Chem Soc.*, 1898, lxxiii. 554 ; 1899, lxxv 423 ; 1901, lxxix. 361). The formation of glucose and pentosans is also suggested.

Incidentally it may be noted here that the formation of w-bromomethyl furfuraldehyde from cotton has been considered of much importance by several who have proposed formulæ for cellulose The production of this substance has been pointed to as proof of the presence of ketonic groups within the cellulose molecule Recently, however, Hibbert and Hill (*Journ Amer. Chem Soc.*, 1923, xlv 176) have shown that w-bromomethyl furfuraldehyde can be obtained in considerable quantities by the action of dry hydrobromic acid on dextrose and its derivatives. The formation of this compound can therefore no longer be regarded as definite evidence that cellulose contains ketonic groups.

Vignon has suggested the formula

$$\begin{array}{ccc} C & & CH \\ | & & O \quad\rangle (CHOH)_3 \\ CH_2 & & CH \end{array}$$
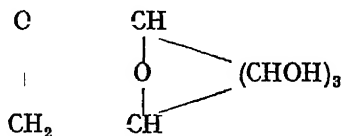
which contains three hydroxyl groups, thereby explaining the nitration of cellulose in which the highest nitrate obtained is tri-nitro cellulose.

Subsequently, Green (*Zeits. Farben-u Textil-Chem.*, 1904, iii. 97) proposed another formula :

$$\begin{array}{c} CHOH\text{---}CH\text{---}CHOH \\ | \qquad\quad O \quad\ O \\ CHOH\text{---}CH\text{---}CH_2 \end{array}$$
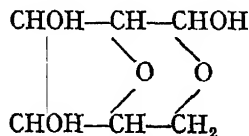
which also postulates three hydroxyl groups. It thus became necessary to determine whether a tetra-acetyl derivative of cellulose was capable of existence ; this was necessary before a decision between the formulæ of Cross and Bevan and of Green could be made Subsequently, therefore, Green and Perkin (*Journ. Chem Soc.*, 1906, lxxxix. 811) carefully acetylated cellulose regenerated from viscose and established by different methods of saponification that only a tri-acetate was obtainable.

Green states that his formula agrees with the following relevant facts ·

1. The highest stage of nitration of cellulose (calculated on the C_6 formula) is the tri-nitrate.

2. The highest acetylation product (contrary to the view of Cross and Bevan) is the tri-acetate.

3. Cellulose forms with concentrated sodium hydroxide a sodium compound (see page 87) which is decomposed with water, leaving the cellulose as a hydrated product. In this latter form it is much more readily soluble in a solution of zinc chloride or ammoniacal copper sulphate.

4. On treatment of the sodium derivative of cellulose with carbon bisulphide, a cellulose xanthate (see page 114) is obtained, readily soluble in water. This product is very unstable, and is decomposed by acids, acid salts, ammonium chloride, or heat with regeneration of a hydrated cellulose.

5. Cellulose does not react with phenylhydrazine or with hydroxylamine ; therefore it apparently does not contain free carbonyl (aldehyde or ketone) groups. On the other hand, by subjecting it to simple hydrolysis, derivatives containing free carbonyl groups are obtained

6. Cellulose yields dextrose as the end product of hydrolysis (for example, with sulphuric acid)

7. Cellulose yields w-bromomethyl furfuraldehyde on treatment with hydrobromic acid in ether or chloroform solution.

8. The oxidation of cellulose gives oxycellulose, a body of marked acid character, which yields furfuraldehyde on distillation with dilute hydrochloric acid

9 On heating oxycellulose with calcium hydroxide, iso-saccharic and dioxybutyric acids are formed

10. The nitrocelluloses when treated with dilute caustic soda yield hydroxypyruvic acid.

The aldehydic character which cotton may develop on restricted hydrolysis is shown thus ·

$$
\begin{array}{ccc}
CHOH-CH-CHOH & CHOH-CH-CH(OH)_2 & CHOH-CH-CHO \\
| \quad\quad\quad O \quad O \quad +H_2O & \quad\quad\quad O \quad\quad -H_2O & \quad\quad\quad O \\
CHOH-CH-CH_2 \quad\longrightarrow & CHOH-CH-CH_2OH \quad\longrightarrow & CHOH-CH-CH_2OH
\end{array}
$$
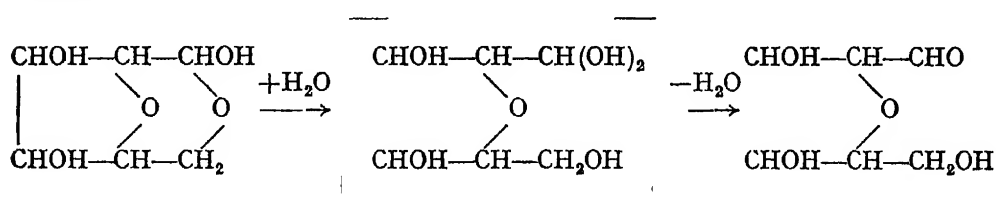
and the formation of alkali cellulose thus :

$$
\begin{array}{cc}
CHOH-CH-CHOH & CHOH-CH-CHONa \\
| \quad\quad\quad O \quad O \quad +2NaOH\longrightarrow & \quad\quad\quad O \quad\quad +2H_2O \\
CHOH-CH-CH_2 & CHOH-CH-CHONa
\end{array}
$$
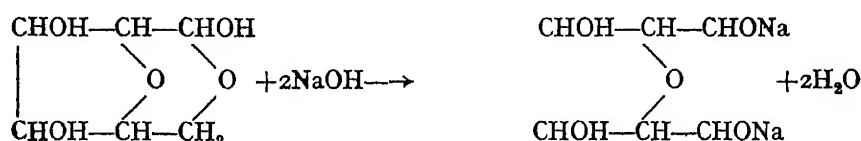
Tollens proposed the following formula :

$$CHO{-}(CHOH)_3{-}CH{-}CH_2 \qquad\qquad O{-\!-}CH{-}(CHOH)_4{-}CH_2OH$$

$$CH{-\!-\!-}(CHOH)_3{-\!-\!-}CH{-}CH_2$$
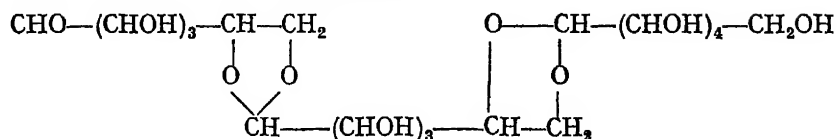
and Barthelemy the following .

$$
\begin{array}{c}
CH_2OH \qquad O \qquad OH \quad OH \\
CH - CH - CH - CH - CH \\
O{<} \qquad\qquad\qquad {>}O \\
CH - CH - CH - CH - CH \\
CHOH \ CHOH \quad O \qquad CH_2OH
\end{array}
$$
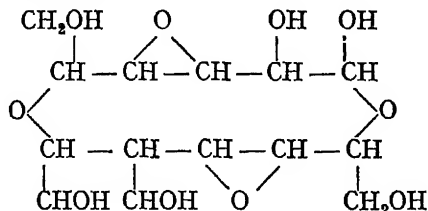
In a very informative and useful review of literature relating to the constitution of cellulose (*Journ Ind Eng Chem.*, 1921, xlii 256) Hibbert cites considerable support for a new formula .

$$
\begin{array}{c}
CH_2OH \\
CH{-\!-}CH{-\!-}O \\
O \\
CHOH{-}CHOH{-}CH
\end{array}
$$
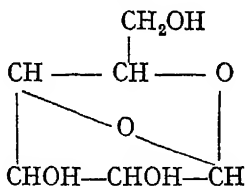
About the same time, Hess (*Zeit Elektrochem*, 1920, xxvi. 234) suggests a formula for cellulose which would suggest that it is a glucoside thus .

$$
\begin{array}{l}
{-}CH{-}O{-}CH{-}CHOH{-}CHOH{-}CH{-}CHOH{-}CH_2OH \\
\qquad\qquad\qquad O \\
CH{-}O{-}CH{-}CHOH{-}CHOH{-}CH{-}CHOH{-}CH_2OH \\
O \qquad\qquad\qquad O \\
CH{-}O{-}CH{-}CHOH{-}CHOH{-}CH{-}CHOH{-}CH_2OH \\
\qquad\qquad\qquad O \\
{-}CH \\
CH{-}O{-}CH{-}CHOH{-}CHOH{-}CH{-}CHOH{-}CH_2OH \\
\qquad\qquad\qquad O \\
CH_2{-}O{-}CH{-}CHOH{-}CHOH{-}CH{-}CHOH{-}CH_2OH \\
\qquad\qquad\qquad O
\end{array}
$$
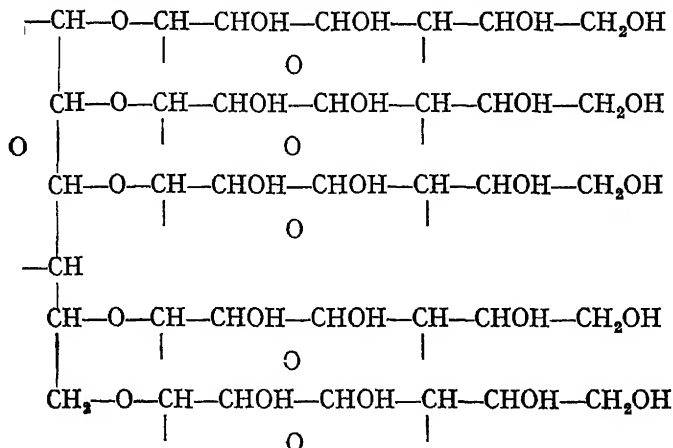
Before dealing further with these suggested formulæ, it will now be convenient to deal with the relationship between cotton and glucose. From the

earliest times it has been known that by treatment of cotton with acids, glucose can be obtained and isolated as such, or recognised by the reducing power and optical rotation of its aqueous solutions. It therefore became a matter of prime importance to ascertain the maximum amount of pure glucose which could be obtained from cellulose. From the following equation it is evident that 100 parts of cellulose should yield 111·1 parts of glucose

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$
$$n \times 162 \quad \longrightarrow \quad n \times 180$$
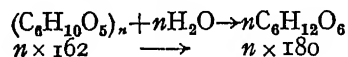
With this purpose in view, Ost and Wilkening (*Chem Zeit*, 1910, xxxiv 461) hydrolysed cotton by means of sulphuric acid, and then estimated the resulting glucose by means of a polarimeter and also by means of Fehling's solution. Both methods yielded closely agreeing results, which were further confirmed by fermentation of the glucose to alcohol and estimation of this. In most of the experiments the yield of glucose from 100 parts of cellulose was greater than 100 parts, and in one instance reached 113·5 parts It was therefore concluded that cellulose could be almost quantitatively converted into glucose, and Flechsig's claim (*Zeit. physiol Chem.*, 1883, vii. 523) to have obtained 95–98 per cent. of the theoretical amount of glucose from cellulose was therefore largely confirmed.

Subsequently, Willstatter and Zechmeister (*Ber*, 1913, xlvi 2401) discovered that cellulose was readily soluble in aqueous solutions of hydrochloric acid containing about 41 per cent. of HCl, and that on prolonged standing hydrolysis of the cotton takes place. By polarimetric methods and the use of Fehling's solution, these workers showed that about 95 per cent. of the theoretical amount of glucose may be obtained from cellulose.

Although the quantitative production of glucose from cellulose thus appeared as proved, the evidence was open to criticism, since it depended only on the measurement of reducing power or optical rotation, and in no instance was the glucose actually isolated in a pure crystalline form Such criticism was further strengthened when Cunningham (*Journ. Chem Soc.*, 1918, cxiii 173) found that such widely different types of cellulosic material as cotton and esparto yielded solutions, by the method of Willstatter and Zechmeister (*supra*), having approximately the same optical rotation. Doubts on this cellulose-glucose relationship were later settled by investigations of Monier-Williams (*Journ Chem. Soc.*, 1921, cxix 803), Irvine and Soutar (*Journ Chem Soc*, 1920, cxvii. 1489) and Irvine and Hirst (*Journ Chem Soc*, 1922, cxxi 1585)

Monier-Williams repeated the work of Ost and Wilkening thus ·

10 g. of cotton wool (containing 6·93 per cent of moisture) were dissolved in 50 c c. of 72 per cent. sulphuric acid, and the dark-coloured viscous solution allowed to remain for one week at ordinary temperature. After dilution to five litres with water, the product was then boiled for 15 hours with reflux condenser. Traces of volatile fatty acids distilled into the condenser, and a small amount of a dark-coloured flocculent precipitate formed within the solutions. The product

13

was afterwards filtered, whereby an almost colourless solution was obtained ; and this was then neutralised with barium carbonate, filtered and evaporated to dryness under reduced pressure. Subsequently, the product was extracted with methyl alcohol (free from acetone), decolourised with animal charcoal and evaporated A residue of crystalline and almost white glucose was thus obtained, and this was subsequently recrystallised and identified as glucose. No other product of hydrolysis could be detected, and it was therefore concluded that about 91 per cent. of the theoretical quantity of pure crystalline glucose could be obtained from cellulose

Irvine and Soutar (*supra*) hydrolysed cotton by means of a mixture of acetic anhydride, acetic acid and sulphuric acid, and then simultaneously hydrolysed and methylated the pioduct by heating it with methyl alcohol containing 0·5 per cent. of hydrochloric acid In this manner cellulose was converted into methyl glucoside, and this was isolated in a crystalline condition and shown to be convertible into glucose. A typical result obtained in this investigation is shown thus

Solid acetylated
cellulose
112 0141 g

Pure
Cellulose.
65·0614 g.

De-acetylated
product somewhat re-
sistant to hydrolysis.—
29·0830 g

Methylglucoside.
34·0513 g.
25 9639 g.
6·2340 g.

Total 66·2492 g.

Acetylated cellulose
soluble in aqueous
acid solution.
10 litres.

so that

Cellulose   ⟶   Methylglucoside   ⟶   Glucose.
100 g.   101·8257 g. equivalent to 94·4775 g.
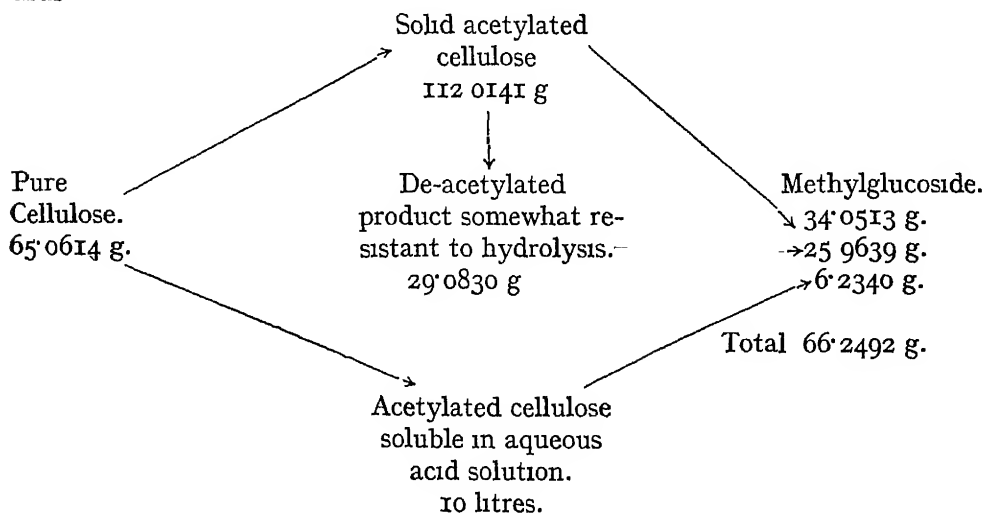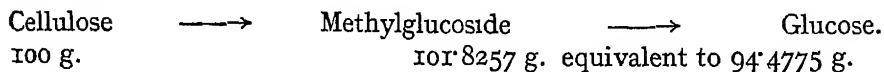
It was thus shown possible to obtain from cellulose 85 per cent of the theoretical amount of glucose in the form of pure crystalline methylglucoside

Two years later, Irvine and Hirst (*supra*) found that the yield of methylglucoside from cellulose could be considerably improved if the acetylation was carried out by the method of Barnett (see page 96), and followed by hydrolysis and methylation with methyl alcohol containing 0.75 per cent of hydrogen chloride. In this manner they obtained the following results .

Cotton.
100 parts.

↓

Cellulose tri-acetate
177 parts.

↓

a and β Methylglucosides
114 1 parts.

equivalent to

↓
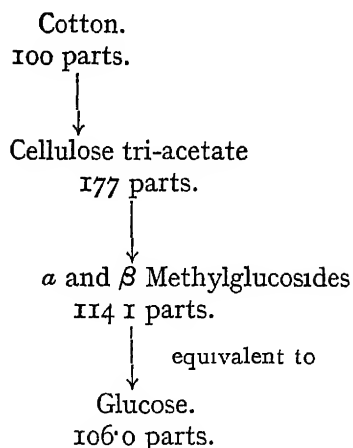
Glucose.
106·0 parts.

Hence 95·1 per cent. of the theoretical quantity of glucose (in the form of pure crystalline methylglucoside) was obtained from cellulose

Further facts bearing on the constitution of cellulose have been obtained by examination of cellobiose, a substance first isolated in the form of its octa-acetate by Franchimont and later studied by Maquenne and Goodwin (*Bull Soc chim.*, 1904, III. xxxi. 854) This substance is related to cellulose in much the same manner as maltose is to starch Thus, cellobiose has been observed as one of the degradation products when cellulose is acted upon by bacteria (Pringsheim, *Zeit. physiol Chem*, 1912, lxxviii. 266). A convenient method for obtaining cellobiose octa-acetate from cellulose is described by Haworth and Hirst (*Journ. Chem Soc.*, 1921, cxix 193)

20 g. of dry filter paper are stirred in a water-cooled mixture of 80 c.c. of commercial acetic anhydride (85–95 per cent) containing 11 c c of concentrated sulphuric acid, so that the temperature is maintained below 20° C. After about 5 minutes the resulting paste is heated in a calcium chloride bath at 120° C. The paste rapidly changes to a dark red mobile liquid, begins to boil at about 112° C , and then commences to turn black At this point the mixture is poured into 1½ litres of cold water and a pale yellow precipitate of cellobiose octa-acetate is obtained This precipitate should dissolve in boiling alcohol but not in cold alcohol, and it is recrystallised from 90 per cent ethyl alcohol. About 25–35 per cent yield calculated on the weight of cellulose is usually obtained

When 10 g of cellobiose octa-acetate are moistened with absolute alcohol, and then stirred with 12 g of caustic potash dissolved in 50 c c of alcohol, it is converted within 2 hours to potassium cellobiosate, and from this pure cellobiose may be prepared by the method of Maquenne

From the methods of formation of cellobiose it is extremely likely that the substance forms part of the cellulose molecule, so that the establishment of its constitution by Haworth and Hirst (*supra*) is very useful

These workers first methylated potassium cellobiosate by means of methyl sulphate and aqueous caustic soda, whereby hexamethyl methylcellobioside was produced, and this by further treatment with silver oxide and methyl iodide was further methylated to heptamethyl methylcellobioside, a substance having the formula—$C_{12}H_{14}O_3$ (OMe)$_8$.

By hydrolysis of heptamethyl methylcellobioside with 5 per cent. hydrochloric acid at 80°–95° C., a clear yellow syrup was produced, and this was shown to contain about equal amounts of tetramethyl glucose and a trimethyl glucose. The latter was proved to be identical with the 2 3 6 trimethyl glucose previously obtained by Denham and Woodhouse (*Journ Chem. Soc.*, 1914, cv. 2364) from methylated cellulose By less drastic hydrolysis, only one methyl group (that protecting the end labile and reducing hydroxyl of cellobiose) may be removed. These facts, assuming the following formula for heptamethyl methylcellobioside, are explainable thus

Heptamethyl methylcellobioside

Limited hydrolysis.

Tetramethyl glucose

Further | Hydrolysis

2 3 6 trimethyl glucose.

There is thus evidence that the molecule of cellulose contains the following cellobiose structure :

$$CH_2OH$$
$$|$$
$$\text{—CH——O—CH}$$
$$|\qquad\qquad|$$
$$O\ \ CHOH\ \ \text{—CH}$$
$$|\qquad\qquad|$$
$$CHOH\quad|\ \ CHOH$$
$$|\qquad O\quad|$$
$$\text{—CH}\qquad|\ \ CHOH$$
$$|\qquad\qquad|$$
$$CHOH\ \ \text{—CHOH}$$
$$|$$
$$CH_2OH$$

Cellobiose,

and this formula for cellobiose has now been confirmed by Bergmann (*Naturwiss.*, 1921, ix 308) and Karrer (*Naturwiss* , ix 1921, 399)

Investigation of the products obtained by methylating cellulose has also yielded valuable information concerning the structure of cellulose. Denham (*Journ Chem Soc.*, 1913, ciii 735 ; 1914, cv. 2357) succeeded in producing by the successive methylation of cotton, by means of caustic soda and methyl sulphate, a fibrous cellulose product containing 25 per cent of methoxyl. From this, after solution and hydrolysis with hydrochloric acid by the method of Willstatter and Zechmeister, a crystalline trimethyl glucose was obtained which was shown to be identical with 2.3.6 trimethyl glucose   Subsequently, Denham carried the methylation further, so that the product contained 44·6 per cent of methoxyl, and Irvine and Hirst (*Journ Chem Soc.*, 1923, cxxiii 518) confirmed the production of the 2.3.6 trimethyl glucose, as the only sugar formed on hydrolysis.

This evidence suggests that the cellulose molecule contains a glucose residue linked in the 1· and 5· positions thus

$$\text{—CHOH}\qquad\qquad\qquad\text{—CHO}\qquad R^1$$
$$|\qquad\qquad\qquad\qquad\quad|$$
$$O\ \ CHOMe\qquad\qquad\ \ CHOH$$
$$|\qquad\qquad\qquad\qquad O\ |$$
$$CHOMe\qquad\qquad\ \ CHOH$$
$$|\qquad\qquad\qquad\qquad\quad|$$
$$\text{—CH}\qquad\qquad\qquad\quad\text{—CH}$$
$$|\qquad\qquad\qquad\qquad\quad|$$
$$CHOH\qquad\qquad\qquad\ CHO\qquad R^2$$
$$|\qquad\qquad\qquad\qquad\quad|$$
$$CH_2OMe\qquad\qquad\qquad CH_2OH$$

2 3 6 trimethyl glucose   Glucose residue present in cellulose,
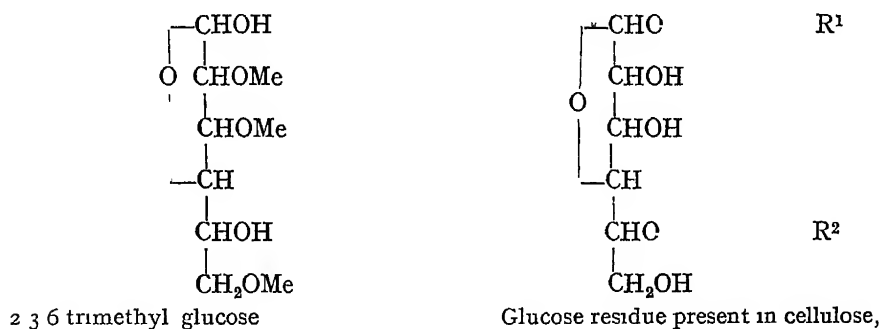
since the latter compound obtained by Denham is most probably trimethyl cellulose (theoretical methoxyl content=45·6 per cent.).

Attempts to methylate cellulose further have not been successful, and it therefore seems probable that trimethyl cellulose contains no free hydroxyl groups It is a solid substance resembling cotton in appearance and in its resistance to various reagents

In a later paper, Irvine and Hirst (*Journ Chem Soc*, 1923, cxxiii. 521) describe further work on trimethyl cellulose, review previous work and deduce a formula for cellulose which is most likely to be accepted as accurately representing known facts.

These workers first prepared a trimethyl cellulose containing 43·8 per cent. of methoxyl, and then subjected it to hydrolysis with methyl alcohol containing I per cent. of hydrogen chloride The resulting methyl glucosides were very carefully examined and trimethyl glucoside alone was found No isomerides were present, and tetramethyl glucose, monomethyl glucose, glucose and sugars were definitely shown to be absent

The quantitative results obtained were as follows

Cellulose.
↓
Trimethyl cellulose   77   per cent. yield.
↓
Trimethyl glucoside   91·5   ,,   ,,
↓
Trimethyl glucose   86   ,,   ,,
(crystalline)

The relationship between cellulose and glucose is then summarised as follows

CELLULOSE

(a)	(b)	(c)	(d)
(Irvine & Soutar, *supra.*) (Irvine & Hirst, *supra*)	(Denham & Wood-house, *supra*), (Irvine & Hirst, *supra*)	(Haworth & Hirst, *supra*)	(Monier - Williams, *supra*); (Willstatter and Zechmeister, *supra*), (Ost & Wilkening, *supra.*)
↓	↓	↓	
Triacetyl cellulose.	Trimethyl cellulose	Cellobiose.	
↓	↓	↓	↓
Methylglucoside	Trimethyl methyl-glucoside	Octa-methylcello-biose	GLUCOSE.
↓	↓	↓	
GLUCOSE	2.3.6 TRIMETHYL GLUCOSE.	2 3.6 TRIMETHYL GLUCOSE.	

Then, in consideration of the fact that only one cellobiose is known, and that 50–60 per cent. is the highest yield of this yet obtained from cellulose, the following is the simplest possible formula for the unit of cellulose :

$$
\begin{array}{l}
\text{CH}_2\text{OH} \qquad\qquad \text{O} \\
\text{—CH——O——CH——CH——CHOH—CHOH—CH} \\
\qquad \text{CHOH} \\
\text{O} \qquad \text{CHOH} \qquad\qquad\qquad \text{O} \\
\text{—CH} \\
\text{CH——O————CH—CHOH—CHOH—CH—CH – CH}_2\text{OH} \\
\text{CH}_2\text{OH} \qquad\qquad\qquad \text{O} \\
\qquad\qquad\qquad \text{Cellulose.}
\end{array}
$$
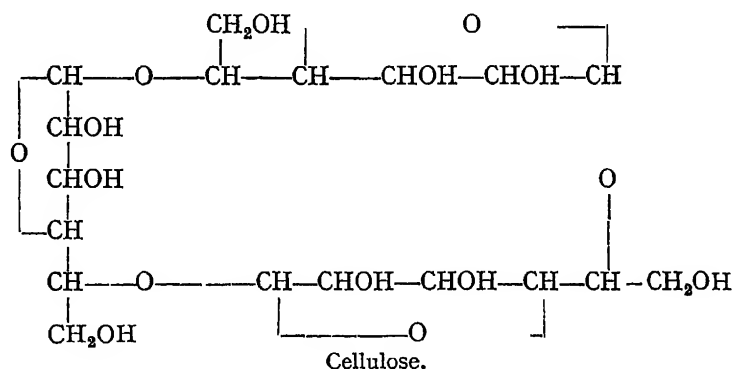
Irvine and Hirst (*supra*) state that they base the above formula on the following facts taken in conjunction

(1) One fragment of the cellulose molecule consists of 1·5 anhydroglucose (Denham)

(2) The fragment is present in cellobiose, which is thus an integral part of the cellulose molecule (Haworth and Hirst).

(3) All the glucose residues in cellulose are identical (Irvine and Hirst).

The formula will stand or fall according as these facts represent the truth, the whole truth, and nothing but the truth , but whatever the case, its elucidation is a distinct credit to all those investigators mentioned above, and particularly to those associated with the University of St Andrews

CHAPTER IX

CELLULOSE AND ITS TECHNICAL IMPORTANT MODIFICATIONS

IN 1734 Réaumur, the French botanist and physicist, suggested the possibility of manufacturing artificial silk thus · " Silk is only a liquid gum which has been dried , could we not make silk ourselves with gum and resins ? This idea, which would appear at first sight fanciful, is more promising when examined more closely." Yet it was not until 1891 that Comte Hilaire de Chardonnet commenced the first process of manufacture at Besançon Now, the production of artificial silk is greater than that of natural silk.

Chardonnet silk was made from nitrated cotton, but three other processes have been developed and compared with these ; the Chardonnet process is now of little importance In spite of this, however, Chardonnet silk is still being made on the Continent in those localities where conditions allow its production at a competitive price. To-day the viscose process appears to be in greatest use for the manufacture of artificial silk.

The following artificial silks are now being manufactured

> Chardonnet silk
> Cuprammonium or cuprate silk.
> Viscose silk.
> Cellulose acetate silk

In the production of either of these kinds of silk, a solution of cellulose is forced through small jets, and the issuing streams of solution are immediately hardened by passage through a coagulating liquor or by simple evaporation in air of the solvent, and the resulting plastic filaments are afterwards washed, bleached and dried to fine threads closely resembling natural silk. The different processes of manufacture are distinguished mainly in the methods by which the cellulose solutions are prepared, and except in the case of acetate silk, the artificial silk produced consists of pure cellulose.

In the manufacture of Chardonnet silk, cotton is nitrated at 40° C., by means of an acid mixture containing 44 per cent H_2SO_4, 38 per cent. HNO_3 and 18 per cent. of water, to a stage such that the product is soluble in alcohol-ether (60 · 40), and this solution is then squirted through jets. A current of warm air (about 60° C) removes the solvent (which may or may not be recovered) and a filament of nitrated cotton is thereby obtained. This is subsequently denitrated by passing it through a solution of ammonium sulphide or sodium hydrosulphide and is then bleached The operations involved are summarised thus

Cotton.

$\downarrow$ nitration.

Nitrocellulose.

$\downarrow$

Solution (approx. 20 per cent) of nitrocellulose in alcohol-ether.

$\downarrow$ spinning.

Nitrocellulose filaments.

$\downarrow$ de-nitration.

Raw cellulose filament.

$\downarrow$ bleaching

Chardonnet silk
(pure cellulose containing about 0·05 per cent. nitrogen).
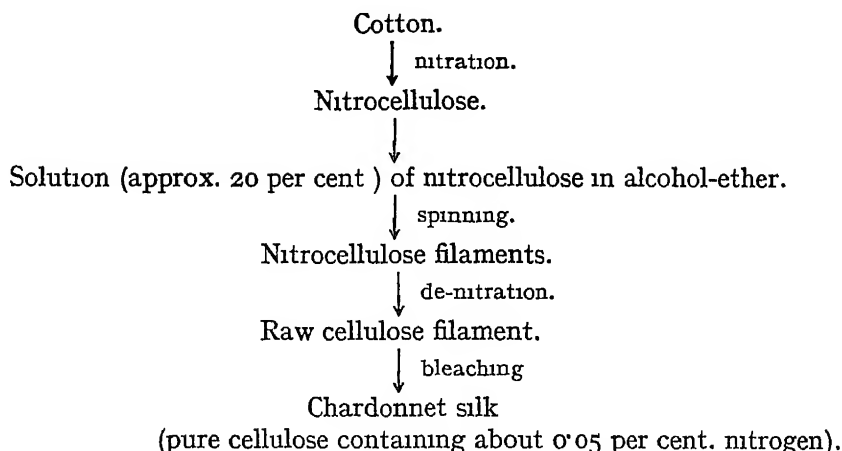
The cuprammonium process was also suggested by a Frenchman—Despaissis —but he died before completing his patent   Subsequently Pauly patented the process in 1897, and afterwards it was developed by the Vereinigte Glanzstoff Farb Akt Ges of Elberfeld   In this process cuprammonium, solution containing about 3 per cent of copper and 8 per cent of ammonia, is used as a solvent for cotton, and the squirted filaments are coagulated in a bath containing sulphuric acid or caustic soda or similar electrolyte   The stages of manufacture are shown thus :

Cotton.

$\downarrow$

Cuprammonium solution of cotton

$\downarrow$ spinning.

Raw cellulose filament.

$\downarrow$ bleaching

Cuprammonium silk
(pure cellulose).
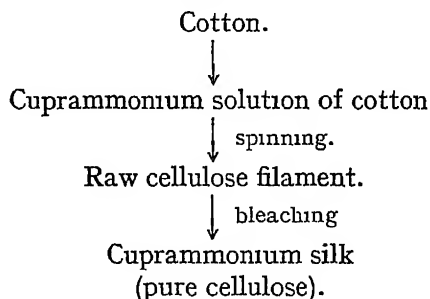
Viscose silk, which now threatens to displace other kinds of silk, was first suggested and patented by Cross, Bevan and Beadle in 1892, and is prepared by squirting solutions of wood pulp in a mixture of caustic soda and carbon bisulphide The resulting filaments are coagulated in a bath containing sulphuric acid, sometimes together with ammonium sulphate and carbohydrates such as starch or glucose.   Subsequently the filaments are bleached and dried

One or two points concerning the technical preparation of viscose solutions are of interest   The wood pulp (spruce) is used in the form of sheets, and these are steeped in caustic soda of 15–18 per cent and then subjected to pressure, so that it contains about three times its own weight of alkali   The alkaline sheets are then finely crumbled in a special machine and allowed to lie exposed to the air for 1 or 2 days   Oxidation occurs, and this has a favourable effect on the

ultimate viscosity of the viscose solution. Afterwards, the alkali-cellulose is agitated with sufficient carbon bisulphide to form the xanthate (see page 115), and this is then dissolved in caustic soda, allowed to ripen by standing, filtered and converted into filaments   The processes are tabulated thus

<div align="center">

Wood pulp.

↓ Treatment with NaOH

Alkali cellulose.

↓

Cellulose xanthate.

↓ Dissolved in caustic soda

Viscose solution.

↓ spinning.

Raw filaments.

↓ bleaching

Viscose silk
(pure cellulose).

</div>
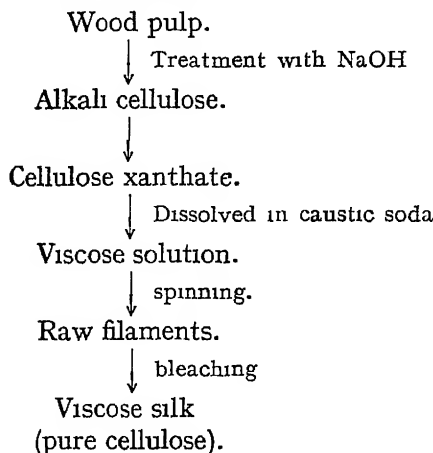
During the war large quantities of cellulose acetate were used for covering and protecting aeroplane fabrics   In England, America and France large factories were erected to produce this product by the method of Drs. Henry and Camille Dreyfus—a method which at that time was being satisfactorily worked in Switzerland. The war over, and the demand for cellulose acetate greatly diminished (solutions of the acetate in organic solvents were commonly known as " dope "), the chief English factory endeavoured to use its plant and organisation for the production of cellulose acetate artificial silk. Consequently, at the present time cellulose acetate silk (the only variety being made in England is known as Celanese ; in America, the silk produced there is termed Lustron) is rapidly gaining in popularity and is being produced at the rate of several tons per week   This silk differs very much from other artificial silks, particularly in its dyeing properties, since it is not pure cellulose, but a cellulose ester

The processes for manufacturing cellulose acetate silk comprise the following :

<div align="center">

Cotton (linters).

↓ acetylation.

Cellulose acetate

↓

Solution of acetate in acetone

↓ Spinning

Raw cellulose filaments

↓ bleaching

Cellulose acetate silk

</div>
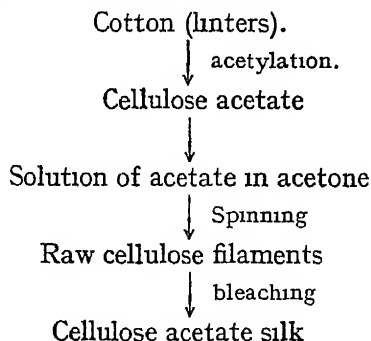
The cellulose acetate is prepared by heating cotton with acetic anhydride, acetic acid and a catalyst (see page 96) such as sulphuric acid or sulphuryl chloride, and the acetate (containing $2\frac{1}{2}$–3 acetyl groups) is freed from the acid constituents of the reaction mixture and subsequently dissolved in acetone. Afterwards the acetone solution is squirted in the usual manner through jets, passed through a coagulating and washing liquor and finally dried. A certain proportion of the acetone solvent is recovered

Natural silk usually has a denier (the denier is denoted by the weight of 9 metres of the silk expressed in grams) of 1–2 ; artificial silks are generally of 6–8 denier and frequently more, though silks of 1–4 denier can be made. Artificial silks also have more lustre than natural silk. In general wearing properties, however, natural silk cannot be equalled by the artificial products

The following estimate of the world's annual production of natural and artificial silks is given by King (*Journ. Text. Inst*, 1923, xiv 225P) for the year ending December 31, 1922

TABLE CIII

Artificial Silk	Production
United States	23,500,000 lb.
England	15,340,000 ,,
Germany	12,584,000 ,,
Belgium	6,292,000 ,,
France	6,292,000 ,,
Holland	2,516,000 ,,
Austria	1,573,000 ,,
Switzerland	1,887,000 ,,
Hungary	1,887,600 ,,
Poland	943,000 ,,
Italy	6,292,000 ,,
Czecho-Slovakia	6,292,000 ,,
Total	79,736,600 lb
Natural silk	59,000,000 lb.

During 1922 the production of artificial silk (mostly viscose silk) was therefore greater than that of natural silk, and in the future it is likely that this difference in production will become even more marked

Apart from differences in dyeing properties, which will be dealt with fully, these four types of artificial silks differ in physical properties. Thus Chardonnet, cuprammonium and viscose silks retain more moisture than cotton, and about three times as much as acetate silk when exposed to the air under ordinary conditions When acetate silk is boiled in water for about 2 minutes, it loses

lustre, shrinks and becomes wool-like ; other silks are not much affected by this treatment. In technical processes it is not advisable to treat cellulose acetate silk in liquors heated above 85°–90° C. ; although Lawrie (*Journ. Soc. Dyers & Col*, 1924, xl. 71) states that this silk is not affected when steamed in an atmosphere saturated with moisture at 100° C.

Cellulose acetate silk has greater heat and electrical insulating powers than other silks, and this may be connected with its small moisture content, which in turn is dependent on its ester character. Further, while all artificial silks lose considerably in tensile strength when wetted, it is claimed for the most recently manufactured acetate silk that its wet strength is equal to its strength when dry. In this connection it is interesting to note a recent process (E.P 213765) by which viscose silk is rendered more resistant to water by a pre-treatment, when dry, with dry chlorine gas or a solution of chlorine in an organic solvent

Constant improvement in the manufacture of artificial silks renders tables of their physical properties liable to become inaccurate, but the following are up to date, the first being compiled by Wheeler (*5th Report of Colloid Chemistry*) and the second by the late L Wilson of Courtaulds Ltd (Beaumont's *Dress, Blouse and Costume Cloths*)

TABLE CIV

Type of Silk.	Raw Material	Tensile Strength		Extension.
		Dry.	Wet.	
Cuprammonium .	Cotton	1·3	0·5	12·5 per cent
,, .	,,	2 16	..	14·1 ,,
Chardonnet .	,,	1·4	0 36	7·5 ,,
,, .	,,	1 48	0·31	15·5 ,,
Viscose .	Wood pulp	1 40	0·55	17·0 ,,
,, . .	,,	1 75	0 75	14 0 ,,
,, . .	,,	1·39	0 47	13 3 ,,
Natural silk .	..	2 5	2 0	21 0 ,,

TABLE CV

Type of Silk.	Tensile Strength		Extension
	Dry.	Wet	
Chardonnet . .	0·75–1·4	0·25–0·6	7·5–16 0 per cent
Cuprammonium . .	1·0 –1·35	0·35–0·55	14·0–18 0 ,,
Cellulose acetate .	1·1	0·7	18 ,,
Viscose . . .	1·2 –1 6	0·45–0·7	11–22 ,,

Chardonnet, cuprammonium and viscose silks are sharply distinguished from cellulose acetate silk by their behaviour towards caustic alkalis. With dilute alkali, acetate silk is slowly converted (according to the temperature of treatment) into pure cellulose by a process of saponification. Under similar conditions, the other silks are only slightly weakened. Viscose silk can be treated in the kier with 1–2 per cent. 2° Tw caustic soda without injury It is advisable, however, to restrict the caustic alkalinity of liquors used in the treatment of the cellulose silks to 0·5 per cent

When treated with caustic soda of mercerising strength (40°–60° Tw) acetate silk is superficially saponified but is not weakened (E.P. 210484/23). On the other hand, pure cellulose silks are disintegrated and partly dissolved, this action being slower at lower temperatures.

Doree (*Biochem. Journ* , 1920, xiv 709) finds that whereas cotton, when immersed in sea water, was found at the end of 3–5 weeks to be completely rotten, cellulose acetate silk was unaffected under similar conditions at the end of 6 months The decay of the cotton was shown to be due to bacterial attack (see page 144), and it therefore appears that such attack is more effective on cellulosic substances (cotton and cellulose artificial silks containing free hydroxyl groups) than on cellulose whose hydroxyl groups have been esterified as in the case of cellulose acetate silk Materials such as fishing-nets, sails, etc., which are frequently immersed in sea water, might therefore profitably be made of acetate silk

Although spinners, weavers and knitters of artificial silks are largely concerned with the physical properties of artificial silks—tensile strength, elasticity and regularity of denier—the dyeing section of the textile industry has found it necessary to carry out considerable research to establish satisfactory dyeing processes for these artificial silks Chardonnet, cuprammonium and viscose silks being pure cellulose, have dyeing properties similar to those of cotton Thus they may be readily dyed with direct, sulphur and vat dyestuffs in the usual manner, although their affinity for these dyes is greater than that of cotton. This greater affinity is probably connected with the higher natural moisture content of these silks Chardonnet silk, however, being prepared from a nitro-cellulose, possesses a distinct affinity for basic dyes and may be dyed with these, although the fastness is improved by previous or after treatment with tannic acid Viscose silk also absorbs basic dyes strongly, but the dyes can be removed by thorough washing. The dyeing of acetate silk is quite distinct from that of the other silks

Those who have to deal with the dyeing of artificial silk fabrics and yarns on the large scale, soon find that the artificial silks as produced by the manufacturers are not uniform in their dyeing properties. Thus, if one portion of a fabric is made from different consignments of silk even from the same manufacturer, it will frequently be found that the silk from one consignment will dye under similar conditions of dyeing to a distinctly lighter or deeper shade than that from another consignment. The resulting effect is that the fabric appeared to have

"bar" effects. This, in fact, constitutes a real difficulty for the artificial silk manufacturers—it is necessary that they should produce a perfectly uniform product.

Wilson and Imison (*Journ Soc Chem. Ind*, 1920, xxxix 322) have found that the affinity of viscose silk for various cotton dyes is affected not only by the method of manufacturing the silk, but also by the molecular complexity of the dyestuffs employed In general, the inequality of different qualities of silk is less evident when dyed with direct dyes of low molecular weight than with those of high molecular weight Further, dyeing at high temperatures is more likely to yield even dyeings than similar dyeing at low temperatures For example, Rosophenine 10B (mol. wt. 600) is even dyeing, but Chlorazol Sky Blue FF (mol wt 992) gives very uneven results Indoine Blue (mol wt 521) is even dyeing, Diamine Green B (mol. wt 812) is fairly even and Chlorazol Fast Pink BK (mol wt 944) is uneven dyeing.

It is therefore possible to classify dyestuffs according to their tendency to emphasise or minimise inequalities in viscose silk, and this has been done by Messrs Courtaulds Ltd. The following lists[1] have been prepared by Messrs. Courtaulds Ltd , and are of considerable value to those who dye this kind of silk ·

DIRECT COTTON DYESTUFFS

Even Dyes.

Benzo Fast Black L
   ,,   ,,   Bordeaux 6BL
   ,,   ,,   Heliotrope BL and 2RL.
   ,,   ,,   Purpurine 4B
Brilliant Benzo Fast Yellow GL
Chlorantine Fast Bordeaux 2RL
   ,,   ,,   Violet BL and 4BL
   ,,   ,,   Yellow 4GL
Chlorazol Black SD.
   ,,   Brown G
   ,,   Fast Black BK
   ,,   ,,   Bordeaux LK.
   ,,   ,,   Helio BK
   ,,   ,,   Red FG, K, A
Chrysophenine G
Congo Orange R
Diamine Aldehyde Bordeaux B
   ,,   Azo Fast Green G.
   ,,   Fast Red F
   ,,   Yellow N.
Diaminogene extra.
   ,,   Sky Blue N.
Triazol Fast Yellow 2G
Diazo Brilliant Orange 5G extra
   ,,   ,,   ,,   GR ,,
   ,,   Fast Scarlet B and BA.

Diazo Fast Violet BL
   ,,   ,,   Yellow G and 2G
   ,,   Indigo Blue 4GL extra.
   ,,   ,,   ,,   3RL ,,
   ,,   Rubine B
   ,,   Geranine B extra
   ,,   Sky Blue 3GL extra
Direct Catechine GR
   ,,   Fast Black B
   ,,   ,,   Orange SE
   ,,   ,,   Violet 2B
Naphtamine Fast Grey B
Naphtogene Pure Blue 4G.
Neutral Grey G
Oxamine Red
Paramine Brown B
   ,,   Fast Red F.
Primuline
Pyrazole Orange G, R, 2R.
Triazogene Orange R
Zambesi Black D.

Moderately Even Dyes

Benzo Fast Heliotrope 4BL.
   ,,   Chromo Brown G

[1] Many dyes exist which are the chemical equivalents of those specified above (*cf* Colour Index).

DIRECT COTTON DYESTUFFS (*continued*)

Moderately Even Dyes (continued).

Benzo Purpurine 10B
Chlorazol Black DV
　,,　　Catechine GR
　,,　　Dark Green PL
　,,　　Fast Yellow B
Diamine Catechine G.
　,,　　Fast Brown G B

Diamine Fast Yellow B.
Diazamine Blue BR
Diazo Brown 3G
　,,　Fast Blue 4GW.
Naphtamine Light Violet 2B.
Oxyphenine 2G, R
Stilbene Orange 4R

Uneven Dyes —All direct cotton blues, including both those of good and moderate fastness to light

Benzo Fast Eosine BL
　,,　　,,　Orange 2RL
　,,　　,,　Scarlet 4BS
Benzoform Green FFL
Chlorantine Fast Brown 2GL, RLZ ⎫
Chlorazol Black BH　　　　　　 ⎪
　,,　　　,,　E extra　　　　 ⎬ In grey and slate shade.
　,,　　　,,　LF　　　　　　 ⎪
Direct Deep Black EW.　　　　　⎪
Diamine Black BH　　　　　　　⎭
Formic Black C
Chlorazol Brown 2G, GM, M and PB
Trisulphon Bronze G
Chlorazol Drab RH

Chlorazol Fast Brown BK
　,,　　　,,　Orange AG and G
　,,　　Eosine B
　,,　　Pink BK
　,,　　Scarlet 4BS
Chromanil Brown 2G.
Congo Rubine
Diamine Catechine 3G
　,,　　Fast Brown G
　,,　　,,　Orange EG and ER.
Diazo Brilliant Green 3G
　,,　Fast Blue GW, 2BW
　,,　　,,　Green BL

When using direct Cotton Dyestuffs for the dyeing of Viscose it should be remembered that

1. The higher the temperature of the dye-bath, the more even is the result.

2. Dyeing in a simple soap bath gives the most even dyeings with those dyestuffs which have an affinity for viscose without the use of Glauber's Salt.

3 The use of Glauber's or Common Salt increases the liability to uneven results, so that their use should be kept down to a minimum

4 When dyeing compound shades, dyestuffs possessing the same degree of evenness in dyeing should be used as far as possible , it is not wise to mix a dyestuff classified as " even dyeing " with one " uneven dyeing," if it can be avoided

BASIC DYESTUFFS

Experience has shown that Basic Dyestuffs in general give more even results on viscose mordanted with Katanol than when mordanted with tannic acid The list overleaf gives the results obtained both on Katanol and tannic acid mordants with various dyestuffs

	Katanol Mordant.	Tannin Mordant.
Acridine Yellow G	Fair.	Fair
Citroflavine 6G	Good	Fairly Good.
Rhoduline Yellow 6G, T	,,	Good
Acronol Yellow T	,,	Fairly Good
Auramine O	,,	Good
,, G	,,	Poor.
Methylene Blue ZF	,,	,,
Cresyl Blue 2BS	Poor	Good
Turquoise Blue 2B	Good	Poor.
Methylene Blue 2B	Poor	,,
Brilliant Rhoduline Blue R	,,	,,
Acronol Brilliant Blue	,,	Very Poor.
Turquoise Blue G	Good.	Poor.
Setoglaucine	Fair	Fair.
Rhoduline Blue GG and 5B	Good	,,
,, Sky Blue 3G	,,	Good.
,, Blue 3GC	Fair.	Poor.
Malachite Green Crystals A	,,	,,
Rhoduline Sky Blue 2B	,,	Fair.
Rhodamine 6G	Fairly Good.	Poor.
Rhoduline Orange RC	Good.	Good.
Brilliant Rhoduline Purple R.	Poor	Poor.
Rhoduline Orange N	,,	Fairly Good.
Rhodamine B	,,	Good.
Rhoduline Red B and G	Good	Fair.
Bismarck Brown	Fair	Poor.
Chrysoidine YRP	,,	,,
Brilliant Rhoduline Red B	,,	Fair.
Rhoduline Heliotrope 3B	,,	Good.
Magenta Crystals	Poor.	Poor.
Methyl Violet 2B	,,	,,
,, ,, 10BL.	,,	,,
Brilliant Safranine BR and G	Good.	Fair
Thionine Blue GO	,,	Poor

Sulphur Dyestuffs

The sulphur dyestuffs, almost without exception, give uneven results on viscose, and their use should therefore be avoided unless the fastness required demands their employment.

The use of Sulphur Blacks for black shades is permissible

VAT DYESTUFFS

Even

Algole Blue 3R.
    ,,   Brilliant Orange FR.
    ,,   ,,   Red 2B
    ,,   ,,   Violet 2B and R.
    ,,   Pink R
    ,,   Yellow R
Caledon Red BN.
Indanthrene Red BN
Duranthrene Red BN.
Caledon Violet RN.
    ,,   Brilliant Purple RR.
Ciba Blue 2B.
    ,, Grey G.
    ,, Pink B
    ,, Heliotrope B.
    ,, Red G.
    ,, Violet B and R
Cibanone Brown V.
    ,,   Green B.
    ,,   Olive B

Cibadone Yellow R
Duranthrene Bordeaux R.
    ,,   Brilliant Violet R.
    ,,   Claret B.
    ,,   Golden Orange Y.
    ,,   Red B
Hydranthrene Violet B.
Hydron Bordeaux B
    ,,   Brown G
    ,,   Green B
    ,,   Olive B and R
    ,,   Pink FB and FF.
    ,,   Scarlet BB
    ,,   Violet B.
Indanthrene Brown 3R
    ,,   Golden Orange G, RN and 3R.
    ,,   Grey B and 3B.
    ,,   Pink B.
    ,,   Violet RR.

Moderately even

Algole Corinth R
    ,,   Olive R
Duranthrene Red 5GY.
    ,,   ,,   Violet 2RN.
Algole Red FF.
Anthraflavone
Caledon Grey KT.

Caledon Jade Green.
Duranthrene Yellow G.
Hydron Bordeaux B.
    ,,   Green G
Indanthrene Golden Orange RRT.
    ,,   Red Violet 2RN.

Uneven.

Algole Blue K
    ,,   Brown G and R.
    ,,   Grey 2B.
Cibanone Orange R.
Duranthrene Orange R.
Hydron Blue G and R

Hydron Brown OG and R.
    ,,   Navy Blue C
Indanthrene Black 2B
Hydanthrene Black 2B.
Caledon Black 2B
    ,,   Green B

Acetate silk, being an ester of cellulose, has no affinity for most of the dyes usually employed for cotton, and new methods of dyeing have been devised to overcome this difficulty   At first, methods of partial saponification were employed, the surface of the silk being thereby converted into pure cellulose, and thus rendered capable of being dyed with direct cotton dyestuffs.   The method adopted by Messrs. Celanese Ltd (E P 169741 of 1921) was carried out thus .

The silk is first cleaned and wetted-out by treatment at 40°–50° C. in a bath containing 2 per cent. of soap and 2 per cent. of 0·880 ammonia (calculated on the weight of silk) for about 20 minutes   It may be remarked here that this treatment is always carried out previous to dyeing whether the silk is or is not

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ultimately saponified. Afterwards, the scoured silk is entered in an alkaline liquor at 75° C. containing 100 gallons of water and 3 lb. of caustic soda of 72° Tw. per 10 lb of silk. This treatment is carried out for 45 minutes, and the superficially saponified silk is then washed in warm water, soured in weak acetic acid, again washed and lightly soaped   It may then be dyed with all kinds of dyes ordinarily suitable for cotton

It was later found that the caustic soda saponification method could be better controlled when such additional substances as silicates, borates and aluminates were present (E P. 175486/20). Subsequently (E P 158340/19) immersion of the silk in 5–25 per cent solutions of a thiocyanate was found to increase its dyeing affinity   These methods, however, have not been seriously developed since they led to the partial destruction of some of the valuable properties of the silk   Investigations were therefore directed to the production of dyes which could be used for dyeing acetate silk without modifying its nature.

It soon became recognised that cellulose acetate silk had an affinity for basic substances and could therefore be satisfactorily dyed by means of basic dyestuffs such as Malachite Green and Safranine   The shades thus obtained are of fair fastness to washing and often to light, and it is not necessary to fix such dyes by an after-treatment with tannic acid as in the case of cotton   In fact, acetate silk has no affinity for tannic acid   Further, it has been found that the affinity of this silk for basic colours is greater when the dyeing is carried out in the presence of Celloxane (Bayer)—a product believed to consist chiefly of zinc nitrate (Lawrie, *Journ. Soc. Dyers & Col.*, 1924, xl 71).

Certain basic dyes have, however, but small affinity for acetate silk, notably Rhodamines and Methylene Blue

Acetate silk was observed capable of absorbing many simple organic compounds such as *p*-nitraniline, aminoazobenzene and *m*-phenylene diamine from aqueous suspension. Thus acetate silk immersed in a warm solution of *m*-phenylene diamine may be afterwards treated with nitrous acid and the absorption of the amine shown by its conversion into Bismarck Brown   Further, the greater the salt-forming power of the organic compound, the less its absorption by the silk. Thus practically all sulphonated aromatic compounds are found to be unabsorbed by cellulose acetate, and this explains why all direct cotton dyes which are made from sulphonated intermediates cannot be applied to acetate silk   This absorbent property of cellulose acetate has proved to be the key to the problem of dyeing   It indicated that suitable dyes for acetate silk would consist of simple coloured aromatic substances containing no strong salt-forming powers, and this line has been speedily developed

In most instances the dyeing of cellulose acetate may be regarded as a process in which the cellulose acetate behaves as an organic solvent, and thereby extracts the organic dyestuff from its aqueous suspension or solution. This theory of the dyeing of cellulose acetate has proved to be more helpful than others in which chemical affinities are considered, although it may be admitted that

the acidic nature of cellulose acetate appears to have an influence in dyeing with basic dyestuffs. It is therefore evidently to be expected, and as is the case, that the dyeing of cellulose acetate is mainly carried out with substances which are but slightly soluble in water.

The small solubility of dyestuffs having an affinity for cellulose acetate has proved to be the greatest difficulty, but it has been overcome by two methods. It has also been found possible to dye cellulose acetate silk by simply immersing it in aqueous suspensions of the dyestuffs, and no difficulties are encountered in the technical application of this method, provided that the particles of the suspension are sufficiently small

The difficulty of solubility was first overcome by Green and Saunders (E P 200873). These workers found that when acetate silk was heated in an aqueous solution containing an acid or alkali, and the methyl-omega-sulphonic acid compound of a primary or secondary aminoazo dyestuff, the acetate silk absorbed the free aminoazo dyestuff as rapidly as it was formed by hydrolysis. For instance, when acetate silk is dyed for 1 hour at 60°–80° C in a bath containing 1 per cent of the dyestuff of the constitution

$$(CH_3)_2N\langle\rangle\!-\!N_2\!-\!\langle\rangle NH\,CH_2\,SO_3Na$$
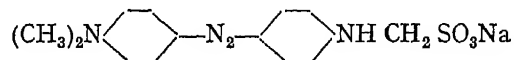
which is obtained by heating unsymmetrical dimethyl-di-p-aminoazobenzene with sodium bisulphite formaldehyde, the silk is dyed a bright yellow.

In a similar manner, acetate silk may be dyed a bright orange shade by means of the following compound

$$NO_2\langle\rangle\!-\!N_2\!-\!\langle\rangle NH\,CH\!\overset{\textstyle CH_3}{\underset{\textstyle SO_3Na}{\diagup\!\!\!\diagdown}}$$
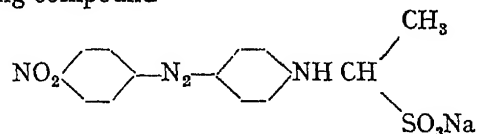
It is therefore obvious that a range of dyestuffs suitable for acetate silk can be obtained by preparation of water-soluble methyl-omega-sulphonic acids of primary or secondary aromatic compounds. Such a range has been placed on the market under the name of Ionamines, and it comprises the following dyestuffs

TABLE CVI

Ionamine			Shade
Ionamine A	.	.	. Yellow.
Ionamine B		.	Orange
Ionamine H	.	.	Yellow
Ionamine L	.	.	Yellow
Ionamine MA	.	.	Golden yellow.
Ionamine KA	.	.	Red.
Ionamine GA	.	.	Terra-cotta red.
Ionamine Blue R		.	Blue with red fluorescence.
Ionamine Blue G		.	Pure blue.

The greater proportion of the Ionamines are prepared from aminoazo compounds ; but it has also been found possible (Green and Saunders, *Journ Soc. Dyers & Col.*, 1924, xl. 138) to prepare them from aminoanthraquinones.

Since in the dyeing operation, the Ionamines are decomposed thus

$$R'.N_2R''.NHCH_2 \diagdown_{SO_3Na} \quad +NaOH \quad \longrightarrow \quad R'\,N_2R''\,NH_2+HCHO+Na_2SO_3$$
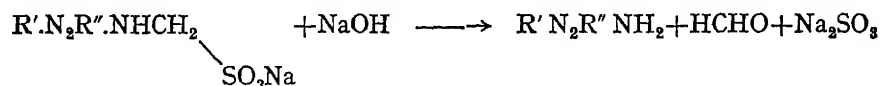
it is evident that when the Ionamine is prepared from a primary amino substance, the dyed acetate silk finally contains this free amine, and can therefore in many cases be further diazotised and coupled with suitable developers   Thus, acetate silk dyed yellow with the methyl-omega-sulphonic acid of unsym-dimethyl-di-*p*-aminoazobenzene may be diazotised and developed in the usual manner with the following results

TABLE CVII

Developer.				Shade
Dimethylaniline	.	.	.	Red
Acetoacetic ether		.	.	Orange
m-Aminophenol	.	.	.	Bluish red.
m-Phenylene diamine		.	.	Maroon
Aminonaphthol (1 7)		.	.	Dark purple.
β-Naphthylamine		.	.	Bluish red
α-Naphthylamine ether		.	.	Purple to black
Phenol	.	.	.	Orange brown
β-Naphthol .		.	.	Purple
β-Hydroxynaphthoic acid	.	.	.	Navy blue to black

Acetate silk dyed with Ionamines may be further developed thus

TABLE CVIII

Method of Dyeing	Ionamine A	Ionamine B.	Ionamine H	Ionamine L.
Direct . .	Yellow	Orange.	Yellow.	Yellow.
Coupled with .				
Naphthol .	Not suitable	Scarlet	Bluish red	Blue violet.
Resorcinol .	,,	Orange brown.[1]	Not suitable	Reddish brown.
Hydroxynaph-thoic acid .	Black.	Red [2]	,,	Blue.

[1] Fastness to washing only fair.   [2] Fastness to washing only good.

Another range of acetate silk dyestuffs discovered and developed by G. H. Ellis has been brought out by Messrs. Celanese Ltd , who have found that when certain aminoazo dyestuffs are heated with 2–3 parts of Turkey red oil, and then poured into water, fairly stable colloidal solutions are obtained, and in these acetate silk can be satisfactorily dyed. The temperature of dyeing is dependent on the stability of the colloidal protection afforded by the Turkey red oil, but in most instances 60°–75° C. is suitable. These dye preparations (10% pastes) are termed S.R A colours, and comprise the following .

TABLE CIX

Dye.			Shade.
S R A Pure Yellow i	.	.	. Lemon
S R.A Pure Yellow ii	.	.	. Greenish yellow.
S R A. Golden Yellow viii	.	.	. Daffodil.
S R A Golden Yellow ix	.	.	. Yellow
S R A. Golden Orange i.	.	.	. Marigold.
S R A Orange i.	.	.	. Tangerine
S R.A. Red i.	.	.	. Scarlet red.
S R A Red iii	.	.	. Crimson red.
S R A. Red v	.	.	. Violet red
S R A Heliotrope i .	.	.	. Heliotrope.
S R A Violet ii.	.	.	. Violet.
S R A Blue iii.	.	.	. Reddish blue.
S R A Blue iv.	.	.	Greenish blue.
S R A Blue v.	.	.	. Deep blue.
S R A Black iii.	.	.	. Jet black.

(Developed with β-hydroxynaphthoic acid)

Turkey red oil is easily decomposed by acids with liberation of the insoluble fatty acid, so that it is essential to apply S R A dyes to acetate silk from an alkaline or neutral solution   If, however, the S R.A dyes are prepared with Monopole soap—a more highly sulphonated castor oil than Turkey red oil—the presence of organic acids in the dyebath is not harmful.

S.R A dyestuffs are easily applied, and their discovery (*Journ. Soc. Dyers & Col* , 1924, xl 285) has solved the difficulties of dyeing acetate silk

Although compounds containing sulphonic acid groups are in most instances not suitable for dyeing acetate silk, it has been found (E P. 202157) that carboxyl groups are not so unfavourable   Consequently, many insoluble dyes suitable for acetate silk may be made water-soluble by introducing carboxyl groups into their molecules

The following soluble aminoazo of this type dyes have been described, as shown on Table CX overleaf.

TABLE CXI

Constitution	Direct.	Developed with β-Naphthol.	Developed with β-Hydroxynaphthoic Acid.	Developed with β-Aminodiphenylamine.
m-aminobenzoic acid + o-anisidine	Yellow	Scarlet.	Magenta	Gold
m-aminobenzoic acid + anthranilic acid	,,	Red	Bluish red.	Olive.
p-aminosalicylic acid + α-naphthylamine	,,	Violet	Reddish blue.	Olive.
5-acetylamino-2-amino-4-methoxytoluene →β-hydroxynaphthoic acid (hydrolysed)	Blue-violet.	Greenish blue	Blue.	Reddish violet
m-aminobenzoic acid → p-xylidine → m-phenylenediamine	Red.	Reddish brown.	Reddish brown	Brown
m-aminobenzoic acid → p-xylidine → α-naphthylamine	Brownish red.	Reddish violet	Reddish blue.	Brown
m-aminobenzoic acid + m-toluidine	Yellow.	Scarlet	Bluish red	
Anthranilic acid + o-anisidine	Orange	Bluish red	Reddish blue	
m-aminobenzoic acid + α-naphthylamine	Reddish orange	Reddish violet.	Reddish blue	
p-aminobenzoic acid + amino-hydroquinone-methyl-ether	Orange	Reddish violet.	Blue	
m-aminobenzoic acid + 4-nitro-2-anisidine.	Greenish yellow.	Reddish orange	Red	
m-aminobenzoic acid + 1-2-aminonaphthol ether	Red	Greenish blue	Bluish green.	

As previously indicated, many anthraquinone compounds can be directly applied to acetate silk from simple aqueous suspension, and the following (E.P. 211720/23) shades can thus be obtained ·

TABLE CXI

Compound	Shade.
α-Aminoanthraquinone .	. Yellow.
α-Methylaminoanthraquinone	Red
1·4-Diaminoanthraquinone	Violet
1·5-Diaminoanthraquinone	Red
Diaminoanthrarufin	Blue
1·4-Aminohydroxyanthraquinone .	Crimson.

Such anthraquinone compounds have been incorporated in a series of Celatene dyes (Messrs Scottish Dyes Ltd.) which comprises the following colours

Celatene Yellow.
Celatene Orange
Celatene Red.
Celatene Red Violet.
Celatene Blue
Celatene Black

Duranol Dyes (British Dyestuffs Corpn. Ltd.) for acetate silk are anthraquinone compounds.

According to E P. 204280, acetate silk may be dyed by means of certain insoluble or difficultly soluble azo colouring matters in the form of their water soluble bisulphite derivatives. Thus acetate silk is dyed golden orange when immersed in an aqueous solution containing the bisulphite compound of aniline azo-β-naphthol together with about 1 per cent. of acetic acid to increase the stability of the dyebath.

Thus, at the present time, acetate silk can be dyed in a large variety of shades, although no direct green dye and only one direct black dye are available Black shades on acetate silk are usually obtained by methods involving the after-treatment processes of diazotisation and coupling, although Clavel (E P. 194840) has indicated that such shades may be directly produced upon acetate silk by oxidation *in situ* of diphenylamine (diphenyl black base).

Apart from the employment of cellulose for the manufacture of artificial silks, cellulose in the form of its esters and ethers is also used for the production of celluloid and plastic compositions These uses are likely to be extended.

Celluloid is manufactured by kneading together under pressure, at about 70° C., a mixture of a cellulose nitrate, camphor and alcohol The conditions under which this is effected are very largely the result of experience rather than scientific investigation, so that technical details are not easily discovered It is, however, known that cellulose nitrates having a nitrogen content of about

11·5–12·3 per cent. are employed, and that higher nitrates are unsuitable. The composition of the mass during kneading is about 2 parts of cellulose nitrate, 1 part of camphor and 1 part of alcohol

After kneading, the plastic mass is moulded or pressed into sheets, rods or shapes as desired, and then allowed to mature for several weeks, during which it suffers contraction owing to loss of volatile solvents employed in its manufacture. The final product is, of course, highly inflammable.

The cellulose esters have already been described (see Chapter V) so that it is only necessary here to draw attention to the cellulose ethers These substances are receiving increasing attention, though as yet expensive to manufacture.

Two principal methods may be employed for the preparation of cellulose ethers The first is that employed by Denham (*Journ. Chem. Soc*, 1921, cxix. 77) in which cotton or cellulose is treated with caustic soda (100 c c of solution contains 20 g of NaOH) and dimethyl sulphate in the ratio of $(CH_3)_2SO_4$ NaOH The reaction is allowed to proceed at about 70° C, and after many methylations a product which may be pure trimethyl cellulose or a mixture of lower ethers is obtained. The formation of trimethyl cellulose probably takes place thus .

$$C_6H_{10}O_5 + 2(CH_3)_2SO_4 = C_6H_7O_2(OCH_3)_3 + H_2SO_4 + (CH_3O)HSO_3$$
$$\text{trimethyl cellulose ether.}$$
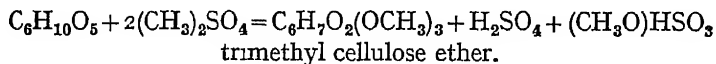
Denham found that the higher the content of methoxyl (OCH_3), the less the solubility of the cellulose ether in Schweitzer's reagent Trimethyl cellulose is practically insoluble in alcohol, acetone and Schweitzer's reagent.

The second method of preparation is that indicated by G P 322586 of 1912, in which alkali-cellulose is heated with about 3 parts of an alkyl iodide under pressure at temperatures exceeding 100° C. Mono-, di- and tri-alkyl cellulose ethers may thus be produced

Those ethers as yet prepared appear to be very inert, and if they are ever used for artificial silks they are likely to remind dyers of their difficulties with cellulose acetate silk. At the present time, however, these ethers appear to find more technical application in the preparation of plastic masses and coating compositions of the celluloid type.

CHAPTER X

SELECTED METHODS OF ANALYSIS

Nitrogen in Cotton.

THE Kjeldahl method is most suitable for the determination of nitrogen in cotton, and since cotton contains about 0·3 per cent. of nitrogen, this, when converted into ammonia, is equivalent to about 2 c.c of N/10 acid per 1 gram of cotton   Ridge (*Journ. Text Inst.*, 1924, xv. 94) has investigated the
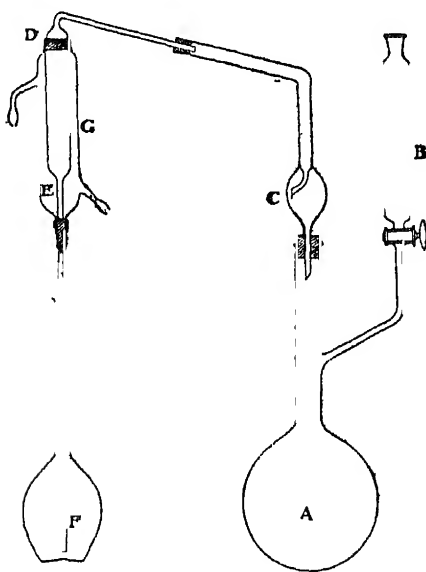
FIG 65 —APPARATUS FOR DETERMINING
NITROGEN IN COTTON
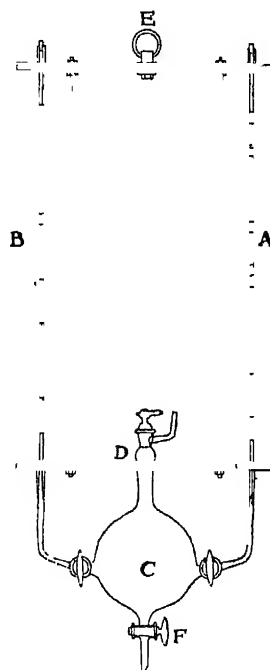
FIG. 66 —ACCURATE TYPE OF
TITRATION APPARATUS

conditions necessary for obtaining accurate results by this method when but 1–2 grams of cotton are available.

With raw cotton, the resulting ammonia may be determined by a titrimetric method   Thus, 1 g of raw cotton, preferably in pastille form (see page 220), is placed with 6 c c of concentrated sulphuric acid and 0 04 c c of mercury in a resistance glass tube about 19 cms in length and 2 5 cms in diameter and having a pear-shaped bulb at one end   The mixture is gradually heated till all signs of froth have disappeared, 2 g of potassium bisulphate are added and the flask again heated until the mixture is colourless   This colourless liquid is then transferred to a distillation flask A (Fig 65) diluted to 200 c c with ammonia-free

water and 35–40 c c. of 40 per cent. potassium hydroxide added so that the mixture becomes alkaline, 1 5–2 c.c of a saturated solution of sodium sulphide are then added, and the mixture is distilled until at least 50 c c. of distillate have passed over. The distillate is collected in bulb C of the special titration apparatus, Fig 66, the leading-in tube F being inserted beneath the surface of an accurately measured volume (2·0–2·5 c c.) of N/10 sulphuric acid. The excess of acid is then titrated by titration with N/10 sodium hydroxide, using methyl red as an indicator. The nitrogen content of the cotton may then be calculated

It should be noted that the distillation flask A has a capacity of 500 c.c., bulb C has a capacity of 150 c c, and that the combined condenser and delivery tube DEF is made of silica, since moist steam is liable to remove alkali from glass.

The titration apparatus (Fig 66) is especially suitable for the titration of small volumes of liquids. It essentially consists of two glass burettes A and B fused into the titration bulb C, the combination being supported by a rigid frame which, during titration, is suspended from a swivel E   The burettes may be accurately read to 0 002 c c

With bleached cottons, 2 g of the material should be similarly digested, except that 12 c c of concentrated sulphuric acid are necessary. The determination of ammonia is then carried out by a volumetric method, which involves the use of a Nessler solution   This reagent is prepared thus :

Solution A —75 g. of potassium iodide are dissolved in 50 c c. of warm water, 100 g of mercuric iodide are then added, and the mixture stirred until solution is complete. The product is diluted to 400 c.c, filtered and then further diluted to 1 litre.

Solution B.—A 10 per cent. aqueous solution of caustic soda free from carbonates and insoluble matter.

The reagent for actual use is prepared by adding 200 c c. of solution B to 300 c.c of solution A, and diluting the mixture to 1 litre

When the digestion of the bleached cotton is complete, the product is distilled as before described, but the distillate is collected in a 50 c c measuring flask. When 40 c c. of distillate have collected, 7·5 c c of Nessler solution are added and the mixture diluted to 50 c c, shaken and immediately filtered from the trace of finely divided metallic mercury which invariably passes over in the distillation and which interferes with accurate colorimetric comparisons. At the same time, similar solutions are prepared by diluting suitable volumes of a standard ammonia solution (1·178 g. of ammonium sulphate per litre) with 7·5 c.c of Nessler solution to 50 c c. When all the solutions have stood for 10 minutes, the standard solution which appears closest in depth to that obtained from the analysis is compared with the latter in a Kober-Klett colorimeter, it then being assumed that the concentrations of ammonia in the two solutions are inversely proportional to the heights of columns which have the same depth of colour.

In both the titrimetric and colorimetric methods it is necessary to do blank

determinations, and make the corresponding corrections.   Ridge has carefully shown that these methods give accurate results

Another method for determining the nitrogen content of cotton is described by Hibbert and others (*Journ. Ind. Eng. Chem*, 1923, xv 750).   3·5 g of cotton are subjected to the Kjeldahl process with 25 c c. of concentrated sulphuric acid and 10 g of anhydrous sodium sulphate and 0·1–0 3 g of powdered copper sulphate, until the mixture is colourless.   Addition of pumice is recommended to avoid bumping.   The product is cooled, diluted with 200 c c of water and made alkaline with 50–70 c c. of a saturated solution of sodium hydroxide   It is then distilled, the distillate (at least 150 c c) being collected in 50 c.c. of N/10 sulphuric acid. Subsequently, the excess of acid is titrated with N/10 caustic soda, and the nitrogen calculated from the result.   Methyl red is used as an indicator in the titration

Phosphorus in Cotton.

The method devised by Geake (*Journ. Text. Inst*, 1924, xv. 81) is found to give consistently accurate results, and is particularly suitable for carrying out a number of determinations with reasonable rapidity.

A quantity of cotton, preferably in pastille form (see page 220), and containing about 0·06 mgm of P_2O_5 (0·12 g. of American or 0·06 g. of Egyptian cotton) is burnt to ash in a porcelain crucible at dull red heat.   The ash is then dissolved in 1 c c of N sulphuric acid, transferred to a centrifuge tube A, Fig. 67, and diluted with 6 c.c of water.   The tube and its contents are then centrifuged for about 5 minutes, so that insoluble matter is thrown to the bottom of the graduated capillary stem.   Two c c of

FIG 67.—CENTRIFUGE TUBE FOR DETERMINATION OF PHOSPHORUS IN COTTON

a special strychnine molybdate reagent are then added from a pipette at the rate of 1–2 drops per second, the mixture being uniformly stirred, either by hand or mechanically by means of the platinum wire C.

After standing for 30 minutes, the tube is centrifuged for 15 minutes at 2500–3000 r.p m (centre of centrifuge to end of capillary stem=18 cms) and the volume of strychnine phosphomolybdate precipitate recorded.   Centrifuging is continued until the volume is constant, and from the final volume the phosphorus content can be calculated, since the tubes are previously calibrated by using, under similar conditions, varying quantities of a standard phosphate solution (0·0575 g of pure anhydrous potassium dihydrogen phosphate in 1 litre of water)   It is also advisable to carry out a check determination with each batch of analysis

The strychnine molybdate reagent is prepared thus ·

Solution A —A filtered solution containing 50 g. of pure ammonium molybdate dissolved in 150 c.c of water

Solution B —Nitric acid of sp. gr. 1·350.   This contains 753 g. of anhydrous acid per litre

Solution C —15 g of strychnine nitrate dissolved in 1 litre of water.

At least one week before use (this period allows of perfect " ripening "), 90 c c of A are added to 270 c.c of B, and to the mixture are added 120 c.c. of C.

Strychnine molybdate is used instead of the corresponding ammonium salt, since the precipitate of phosphomolybdate obtained with the former is about thirty times more bulky than that obtained with the latter.

The centrifuge tube employed had a capillary stem 1 mm. diameter of bore and 5 5 cms long , the upper portion was 3 cms. in length and 2 cms. in diameter.

Fat, Wax and Resin in Cotton.

As indicated in a previous chapter, the methods of extraction of fatty matters from cotton are subject to considerable errors, and for this reason it was suggested by Higgins (*Journ. Soc Dyers & Col*, 1923, xxxix. 150) that a standard method was desirable   Subsequently Fargher, Higginbotham and others (*Journ. Text Inst*, 1924, xv 75 and 120) have established methods for determining the amount and nature of the fats and waxes present in cotton, and it is probable that their methods are more reliable than others, for they are based on a considerable amount of detailed research.

Since hot chloroform appears to be the most inclusive solvent, it is used for the determination of the total fat, wax and resin present in cotton.

A modified Soxhlet apparatus is employed as shown in Fig 68.   It is made of copper and tinned on those surfaces exposed to the vapours of the solvent ; after continued use, even with chlorinated solvents, the metal showed no sign of attack.   The vapour from the boiling solvent passes upwards between the two concentric jackets, thereby maintaining the solvent, in contact with the cotton, practically at boiling-point   The outer jacket is lagged with asbestos as far as the top of the siphon tube

In the determination of fat, wax and resin, 100 g of cotton are extracted for 6 hours with chloroform in the hot Soxhlet apparatus, the chloroform being maintained actively boiling throughout the operation.   In certain instances, where the material available is small, 20 g. of cotton are similarly extracted for 3 hours   The solvent is then distilled from the extract, and the residue is dried to constant weight at 80° C *in vacuo* as produced by a water pump.

It is found that carbon tetrachloride and benzene do not easily remove resinous matters from cotton, so that if the chloroform is replaced, preferably by carbon tetrachloride, an approximate value for the fat and wax content of cotton may be obtained   Since carbon tetrachloride is liable to contain traces of chlorinated products, this solvent, before use, is twice distilled over paraffin wax.

A = Soxhlet

B = Condenser

C = Siphon Tube

Ordinary type Soxhlet.   Hot type Soxhlet
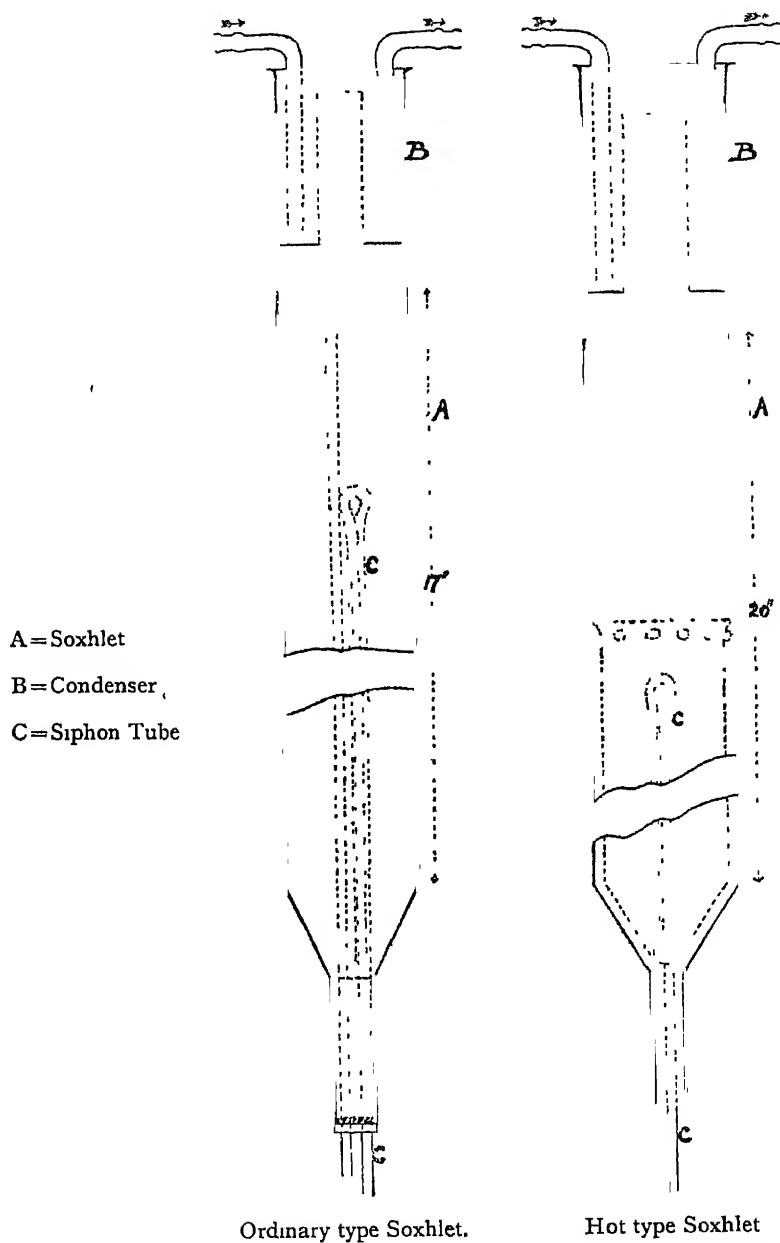
FIG. 68.—SOXHLET APPARATUS FOR DETERMINING
FAT IN COTTON.

The examination of the extract is shown to be possible even if but 0·3 g is available, and this may usually be obtained from 100–300 g. of raw cotton, sized yarn or fabric, or from 800–1000 g. of scoured and bleached cotton   Generally, a fat or wax is characterised by its saponification value, unsaponifiable matter content, acid, acetyl and iodine values

In the determination of the saponification value, 0·1–0·2 g. of the extract is heated for 4 hours with 10 c c. of an N/10 solution of potassium hydroxide in a 100 c c. conical flask on a water bath, the flask being attached to a reflux condenser.   Ten c c. of neutral alcohol and 10 drops of a 0·1 per cent solution of phenolphthalein are then added and the excess of alkali titrated with N/10 hydrochloric acid   It is necessary to keep the products of saponification in solution, and this is accomplished by warming or by addition of more alcohol The saponification value is then calculated in the usual manner, and corrected by a blank determination

Determination of the acid value is made in exactly the same manner except that the boiling is omitted.   When it is suspected that the extract may partly saponify with cold alkali, the acid value must be determined by direct titration For this, 0·1–0·2 g of the extract is dissolved in 10 c c of neutral alcohol, and after the addition of 10 drops of a 0·1 per cent phenolphthalein solution the acidity is titrated with N/10 caustic soda, care being taken to keep the wax substances in solution   A blank determination is necessary.

Unsaponifiable matter is determined by means of the solution remaining after determination of the saponification value   This solution is made alkaline by addition of N/10 caustic potash, and then evaporated to a small bulk in a porcelain dish.   A glass funnel is placed over the dish so that loss by frothing may be avoided   Sodium bicarbonate is then added to combine with the excess of potassium hydroxide and the product then mixed with 5 g of purified and extracted sand   The mixture is evaporated to dryness at 100°–110° C. and extracted in a hot Soxhlet apparatus with light petroleum (b p. 40°–50° C. dried over phosphorus) for 6–8 hours.   The extract thereby obtained is then dried to constant weight at 80° C. *in vacuo*, and this weight represents the unsaponifiable matter.

It will be noted that the petroleum ether should be perfectly dry and that it should not be replaced by ether, since this has a tendency to dissolve soaps

The acetyl value is determined from the saponification values of the wax extract before and after acetylation by means of the formula .

$$A = \frac{S' - S}{1 - \lambda S}$$

where A = acetyl value ; S and S' = saponification values before and after acetylation respectively and λ = a constant = 0·75.   S and S' are expressed in grams and not milligrams.

The method is carried out thus   0·2–0·3 g of the wax extract is heated over a free flame in a Geissler flask with 5 c c. of acetic anhydride for 3 hours Excess of anhydride is then decomposed by boiling the product after dilution with water   The dilute acetic acid thereby produced is then removed by decantation and the process repeated until all acid and anhydride is removed Finally the acetylated product is dried to constant weight at 80° C *in vacuo* and its saponification value determined in the manner previously described.

It is found that the iodine value may be determined in the usual manner if 0·10–0·20 g of wax extract is available, but since cotton wax contains a small proportion of sterols, the method of Hubl is preferable and gives values which differ from those obtained with Hanus' or Wijs solutions   Fargher and Higginbotham do not therefore describe the method fully, but for completeness, details of the Hubl method are given here

0·20 g of the wax extract is dissolved in 10 c c. of chloroform and 25 c.c of Hubl's iodine solution added, the mixture being contained in a stoppered bottle and allowed to stand for several hours protected from light   Then 15–20 c.c. of a 10 per cent solution of potassium iodide is added for the purpose of keeping mercury compounds in solution, and the unabsorbed iodine is afterwards determined by titration with an N/10 solution of sodium thiosulphate, using starch as an indicator   The iodine content of the Hubl solution is determined in a similar manner, the wax being absent, and the amount of iodine absorbed by 100 g of the wax can then be readily calculated and the result is known as the iodine value

Hubl's iodine solution is prepared by mixing two solutions, one containing 25 g of iodine in 500 c c of 95 per cent. alcohol and the other, 30 g of pure mercuric chloride in the same quantity of 95 per cent. alcohol.   The mixed solutions do not keep without change longer than about 24 hours

In cases where the amount of extract is very small, methods described by Gill and Simms (*Journ Ind Eng. Chem*, 1921, xiii. 547) may be employed ; such methods require but 0·01 g of extract for the determination of either iodine or saponification values

The following results were obtained with cotton wax by Fargher and Higginbotham while establishing the above described methods

TABLE CXII

Type of Cotton	Saponification Value	Acid Value	Unsaponifiable Value	Iodine Value (Hubl).	Acetyl Value
American .	65	20–30	52	20·1	73
Egyptian .	76	20–30	48	23·1	63

Copper Number.

The *copper number, cellulose number* and *corrected copper number* which have been referred to as indicating the approximate degree of degradation of a particular sample of cellulose, are related thus :

The purest form of cellulose is capable of retaining *cupric* salts which cannot be removed by washing with hot water but only by solvents, such as ammonia or nitric acid. The number of grams of such copper thus retained by 100 g. of cellulose when subjected to the treatment necessary for the determination of the *copper number* (see later), except that the treatment is carried out in the cold instead of at boiling temperature, is termed the *cellulose number*

When partly degraded cellulose is boiled under the standard conditions for determination of the copper number (see later) it reduces a part of the copper sulphate in the Fehling's solution to *cuprous* oxide and simultaneously absorbs an amount of *cupric* copper salt proportional to its *cellulose number*. The total number of grams of cuprous and cupric copper absorbed per 100 g. of cellulose is termed the *copper number*.

The difference between the copper number and the cellulose number is the *corrected copper number*, and this is a measure of the reducing power of the cellulose under standard conditions

The behaviour of pure and degraded celluloses towards Fehling's solution has been closely studied by Schwalbe, and the following method has been devised by him and is described in his book, *Die chemische Betriebs-kontrolle in der Zellstoff- und Papier-Industrie.*

FIG 69 —SCHWALBE APPARATUS FOR DETERMINATION OF COPPER NUMBER OF CELL-ULOSE

250 c c of distilled water and 2–3 g of the air-dry sample of cellulose are placed in flask A (Fig 68) of 1500 c c capacity and heated to boiling with stirring   B is a condenser through which passes a stirrer.   Then 100 c c. of Fehling's solution are heated to boiling and added to the cellulose through the dropping funnel C, the latter being washed down with 50 c.c of boiling water

The contents of flask A are then gently boiled for exactly 15 minutes with stirring   One gram of purified kieselguhr, in 50 c c of water, is added, and the contents of the flask are then filtered at the pump through double filter paper in Buchner funnel, the residue being washed with hot water until the filtrate is free from copper, as tested by means of a solution of potassium ferrocyanide

Subsequently the contents of the Buchner funnel are heated with 6·5 per

cent. nitric acid on a water bath till the precipitate of cuprous oxide is dissolved The product is then filtered as before, the last traces of copper retained by the cellulose residue being finally removed by washing with a little strong ammonia solution and then hot water   The combined filtrate and wash liquors are then evaporated to a small bulk and the copper content determined by electrolysis. The number of grams of copper thus obtained per 100 g of cellulose is the *copper number*

The *cellulose number* is determined by subjecting a similar sample of the cellulose to the same treatment just described for the determination of the copper number, except that the treatment with Fehling's solution is carried out for 45 minutes in the cold and not for 15 minutes at boiling temperature.   It is thus assumed, though the assumption is doubtful, that the cellulose number is the same, whether determined in the cold or at boiling temperature.

The Fehling's solution is prepared immediately before use by mixing equal volumes of the following stable solutions

Solution A —138·6 g of pure copper sulphate are dissolved in water, diluted to 2 litres and the solution filtered through linen.

Solution B —692 g of pure Rochelle salt and 200 g. of alcohol-purified caustic soda are dissolved together in water, the solution being diluted to 2 litres, and filtered through asbestos

In view of the tedious nature of the Schwalbe method, Knecht and Thompson (*Journ. Soc Dyers & Col*, 1920, xxxvi 255) have introduced two alternative processes

In the first process, the sample of cellulose is subjected to the same treatment with Fehling's solution as described in the Schwalbe method ; but after removal of soluble copper salts, by filtration and washing at the pump, the residue of cuprous oxide and cellulose is immersed in a solution containing 1–2 g of iron alum and some sulphuric acid.   The cuprous copper present reduces its equivalent of iron to ferrous sulphate, and this latter is then directly determined by titration with a standard solution of potassium permanganate

It will be observed that in this method cupric copper is absorbed by the cellulose but it does not affect the permanganate titration, since this only measures the amount of *cuprous* copper present.   The copper number obtained is therefore the *corrected copper number.*

Again, it is evident that the filtrate, containing all the copper salts not absorbed or reduced in the test, can be titrated with titanous chloride, after addition of iron alum and hydrochloric acid, and its copper content determined. The difference between the amount of copper thus determined and the total amount used in the test is thus a measure of the sum of the *corrected copper number* and *cellulose number*   The latter may be easily determined, using the Schwalbe procedure, except that the copper absorbed by the cellulose is estimated by means of titanous chloride in the presence of iron alum.

From these considerations it is evident that the following results obtained

15

by Knecht and Thompson indicate that the method is accurate as well as rapid

TABLE CXIII

Test Number	Corrected Copper Number (KMnO$_4$)	Sum of Corrected Copper Number and Cellulose Number (TiCl$_3$)
1	13·3	13·6
2 . . .	13·0	13·8
3 . . .	13·5	14·1
Average .	13·3	13·8
Cellulose number determined with TiCl$_3$		0·4
Hence, corrected copper number (by calculation) . .		13 4

The second method was devised because it was shown that oxidised cellulose yielded products having no reducing power when boiled with caustic soda, and it was thought that this action may play a part when cellulose is treated with Fehling's solution   A copper solution containing sodium carbonate instead of caustic soda was therefore employed

Such a stable copper solution is prepared by dissolving 100 g of anhydrous sodium carbonate, 200 g of sodium citrate and 125 g of potassium thiocyanate in about 800c.c of water, and then adding a solution containing 18 g of crystalline copper sulphate   The resulting clear solution is then diluted to 1 litre, it being perfectly stable during storage

For determination of the copper number, about 2 g of cellulose are boiled for 15 minutes with 100 c c of the copper solution, 200 c c. of water and 8 g of sodium carbonate.   The product is then filtered and the residue freed from soluble copper salts by thorough washing with hot water.   The residue, consisting of cellulose and insoluble *cuprous* thiocyanate, is treated with warm semi-normal caustic soda, whereby cuprous hydroxide is formed, and thiocyanate is then removed by filtration.   The residue is immersed in an acidified solution of iron alum and the resulting ferrous sulphate determined, after filtration from cellulose, by means of potassium permanganate, as in the first method.   In this manner, the *corrected copper number* is also obtained directly

The results obtained by this method appear to be accurate though slightly higher than those obtained by the first

More recently, Clibbens and Geake (*Journ Text Inst*, 1924, cxv 27) have critically examined the methods commonly in use for determining the copper

number of cellulose and point out that Fehling's solution decomposes to some extent when boiled alone and in the absence of cellulosic matter.   Although the effect of this decomposition on the copper number is small, it is, of course, most evident when the copper number is also small, and this renders the characterisation of very slightly degraded cellulose a difficult matter.   Clibbens and Geake have accepted Braidy's method (*Rev gen. Mat Col*, 1921, xxv 35) as being more accurate, and adapt it in the following process

Fehling's solution is replaced by the following two solutions

Solution A.—An aqueous solution containing 100 g. of pure crystalline copper sulphate per litre

Solution B.—An aqueous solution containing 50 g of sodium bicarbonate and 350 g of crystalline sodium carbonate per litre.

Over 2·5 g of the cellulose sample, contained in a flask of about 100 c c capacity, is poured a boiling mixture of 5 c c. of A and 95 c c of B, and the mouth of the flask is then covered, and the flask immersed for exactly 3 hours in a rapidly boiling water bath   The contents are then filtered and washed, first with dilute sodium carbonate solution and then water, the residue on the filter being then washed with an iron alum solution prepared from

Iron alum	100 g
Concentrated sulphuric acid	. 140 c c
Water . . .	to make 1 litre of solution,

portions of 15, 10 and 10 c c being usually sufficient to remove all the cuprous oxide.   Afterwards, the cellulose residue on the filter is washed with 2N sulphuric acid, and the combined filtrates are titrated with N/25 potassium permanganate.

This method also gives directly the *corrected copper number*.   The composition of the copper solution also leads to the obtaining of very small *cellulose numbers*, for example, 0·01   It is also shown that this method is more sensitive to slightly modified cellulose than the methods of Schwalbe or Knecht and Thompson.

α, β and γ Celluloses.

The original method of Cross and Bevan for determination of *α, β* and γ-celluloses in cotton and other cellulose materials was essentially a gravimetric one   Cellulose was treated with 17 5 per cent cold caustic soda, diluted and filtered.   The residue, freed from alkali, was dried and weighed as *a*-cellulose ; the filtrate was acidified with acetic acid and the *β*-cellulose, thereby precipitated, was filtered off, washed, dried and weighed   The γ-cellulose was calculated by difference

Cross and Bevan's method was subsequently described by Schwalbe (*Die chemische Betriebs-kontrille in der Zellstoff- und Papier-Industrie*, p 221) with modifications by Jentgen and Wæntig.   Recently, however, the determination

of these three types of cellulose has been improved upon as regards rapidity and accuracy by Bray and Andrews (*Journ Ind Eng Chem*, 1923, xv 377)

One gram of the sample of cellulose is treated for 30 minutes in a beaker with 25 c.c of 17·5 per cent cold caustic soda, and the product is then filtered through a Gooch crucible   The residue is washed with 50 c c of 4 per cent. caustic soda, and then with 300 c c of cold distilled water in small quantities It is not necessary to completely free the residue from alkali—a difficult matter.

The residue of *a*-cellulose on the filter is then dissolved in 30 c.c. of 72 per cent sulphuric acid, and the solution diluted with water to 100 c c   Ten c c. of this are added to 10 c c. of a standardised solution of potassium bichromate (containing about 90 g per litre) and 60 c c of 72 per cent sulphuric acid, the mixture being gently boiled for 5 minutes and then cooled with ice   In the oxidation which ensues, cellulose is completely decomposed thus

$$C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O$$
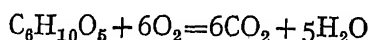
so that the product is then titrated with a solution of ferrous ammonium sulphate From the amount of potassium bichromate reduced, the amount of *a*-cellulose in the original sample may be readily calculated

The filtrate contains β and *a* cellulose. It is therefore divided into two equal portions of 200 c.c. each, one portion being acidified with 5 c.c excess of 10 per cent sulphuric acid (methyl orange being used as an indicator), diluted to 250 c c and allowed to stand for several hours until the precipitated β-cellulose is completely coagulated and settled   Afterwards 25 c c of the supernatant liquor is oxidised (as for *a*-cellulose) at the boil for 5 minutes with 5 c c of potassium bichromate solution and 60 c c. of 72 per cent. sulphuric acid, cooled with ice and the amount of reduction measured by titration with ferrous ammonium sulphate. These results enable the amount of γ-cellulose (soluble cellulose) to be estimated.

The other 200 c.c. portion of the filtrate is diluted to 250 c c , and 25 c c of this are oxidised as described for γ-cellulose, the result enabling the combined amount of β and γ-cellulose present, to be calculated. β-cellulose can therefore be calculated by difference.

Compression of Cotton for Analysis.

The extreme bulkiness of cotton is a serious disadvantage in investigations and processes of analysis   Although cotton has a density of 1·5, it is found that 1 g of loose cotton occupies at least 10 c.c., and may take over 10 c c of liquid to cover it completely   Williams (*Journ. Text Inst.*, 1923, xiv. 295) has therefore designed a convenient press whereby cotton may be compressed into pastille form such that 1 g occupies less than 0 8 c.c. ; such pastilles retain their shape so long as they are exposed to ordinary humidities

Further, these pastilles do not expand when placed in organic liquids such as alcohol , in water, they tend to swell, but this is largely prevented by previously

exposing them for some time to an atmosphere saturated with water vapour. When placed in a flame, the pastilles char and burn, but do not expand.

The press is shown in Fig 69, which is self-explanatory.

Preparation of Cotton Sections.

The following method is described by Clegg and Harland (*Journ. Text. Inst*, 1923, xiv 489)   A bunch of a few hundred combed parallel hairs is bound on a wire frame and immersed in alcohol for two minutes to displace air bubbles   The frame is then placed in water, and then in sufficient of an aqueous hot solution of gelatine to cover it   The whole is maintained warm for 3 hours (the gelatine should remain liquid) and the frame afterwards immersed in 95 per cent alcohol containing 5 per cent of 40 per cent. formalin solution   After several hours, the gelatine becomes hardened, and this process is then completed by placing the frame in absolute alcohol for a few minutes   Subsequently the cotton bundle is embedded in vaseline-paraffin, sections cut with a microtome and mounted in glycerine-jelly. The gelatine solution used should be such that it sets quite stiff when cold.
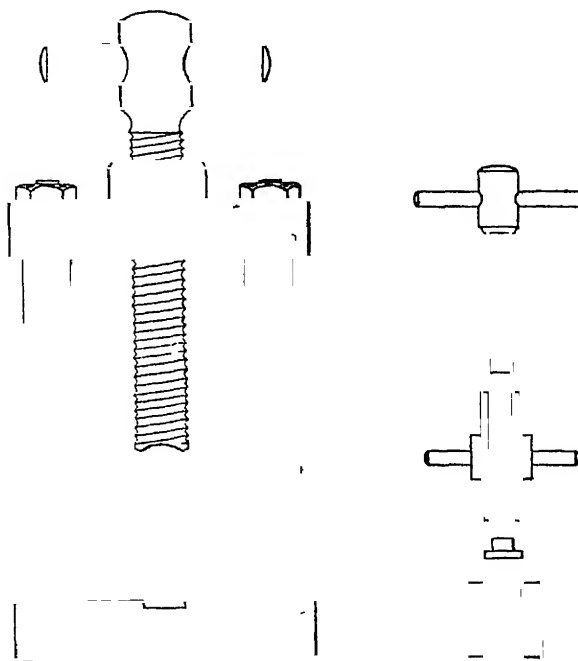
FIG 70 —APPARATUS FOR COMPRESSING COTTON.
(Williams.)

In a method described by Willows and Alexander (*Journ. Text. Inst*, 1921, xii 99) two solutions are employed, one (A) being a viscous syrup containing cellulose acetate dissolved in acetone, and the other (B) containing 5 g. of cellulose acetate dissolved in 100 c c. of acetone.

A microscope slide is painted with a layer of B and then, after drying, with two more layers of A.   A bundle of parallel cotton hairs which have been steeping for 1 hour in B are then placed on the slide and covered with layers of A   The slide is then dried in a dessicator over calcium chloride, and subsequently hung in an atmosphere of acetone vapour   The film thus softens and can be peeled from the slide and embedded in paraffin wax of m.p $40°-45°$ C., thus being suitable for cutting sections
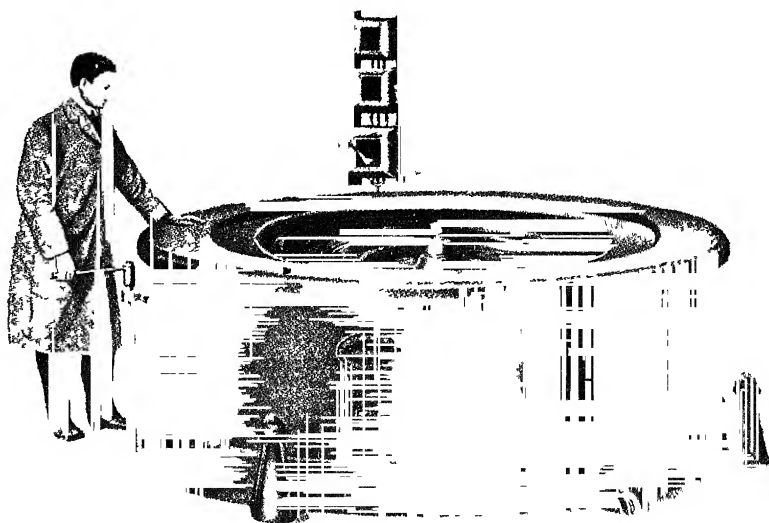
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